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**Removal of
Surface Inactive
Substance By
Foam Separation
Process**

**By
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The Ohio State University
1972**

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REMOVAL OF SURFACE INACTIVE SUBSTANCES BY
FOAM SEPARATION PROCESSES

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ABSTRACT

The major findings of an extensive laboratory investigation of the removal and use of hydrolyzable metals in foam separations are described in this final project report. References to the more detailed published reports of the research are also given. The relationships and mechanisms of the foam separation processes of precipitate flotation, foam fractionation, colloid flotation and microflotation are discussed in terms of the aqueous hydrolytic chemistry of the metals examined. These metals included iron(III), copper(II), zinc(II) and lead(II). Aluminum sulfate was used as the coagulant-aggregating agent for the sol studies with the bacterium Bacillus cereus, the clay illite, and colloidal titanium dioxide. The surfactants used were lauric acid, stearylamine, CTAB and sodium lauryl sulfate which are representative of strongly and weakly ionized cationic and anionic collectors. Solution and operating variables that were studied in a batch experimental system included gas flow rate, pH, temperature, ionic strength, surfactant type, and collector and coagulant concentrations.

Solution pH was found to be the single most important variable. Gas flow rate was shown to affect the rate but not ultimate removal by foam fractionation. Collector concentration had the opposite effect. As compared to the foam separation of ionic species or discrete sol particles the flotation processes for removing metal precipitates or aggregated sols were found to be more efficient and much less dependent on most of the variables examined. In general, the strongly ionized surfactants are more effective than the weak acid or base types, whereas the choice between a cationic or anionic collector is system dependent. A method based on calculations with hydrolysis constants is described for predicting metal removals.

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INTRODUCTION

The removal and concentrating of solutes and particulates by their accumulation at the surfaces of rising bubbles is accomplished by a series of processes known collectively as adsorptive bubble separation techniques (Karger et al., 1967; Lemlich, 1972). The phenomena associated with these processes are important because they can explain the transport of materials in natural aquatic environments such as the sea (MacIntyre, 1970) and because they form the basis for unit operations that are capable of very effectively removing, separating or concentrating the components of complex liquid dispersions. The common feature of these processes is that separation is brought about by virtue of differences in the surface activity of the dispersed ionic, molecular, or condensed substances. These may be naturally surface active or rendered surface active by reaction with a suitable agent called a collector. The surface active components are adsorbed and collect at the interface between gas and liquid phases as qualitatively described by the Gibbs equation.

As indicated in Figure 1, the adsorptive bubble separation techniques may be subdivided into two major classes depending whether or not a foam (or froth) is produced. The non-foaming techniques include solvent sublation (Sebba, 1962; Karger, Pinfeld and Palmer, 1970) and bubble fractionation (Lemlich, 1966). The foam separation methods, which were the subject of the research in this report, utilize a foam phase as an integral part of the process. Two transport mechanisms operate that lead to the subdivision of foam separation into foam fractionation and flotation processes. A further breakdown of the latter is indicated in Figure 1. Foam separation nomenclature was rather chaotic until a scheme such as the one shown in the figure was proposed by several active workers (Karger, et al., 1967). Figure 1 represents a further refine-

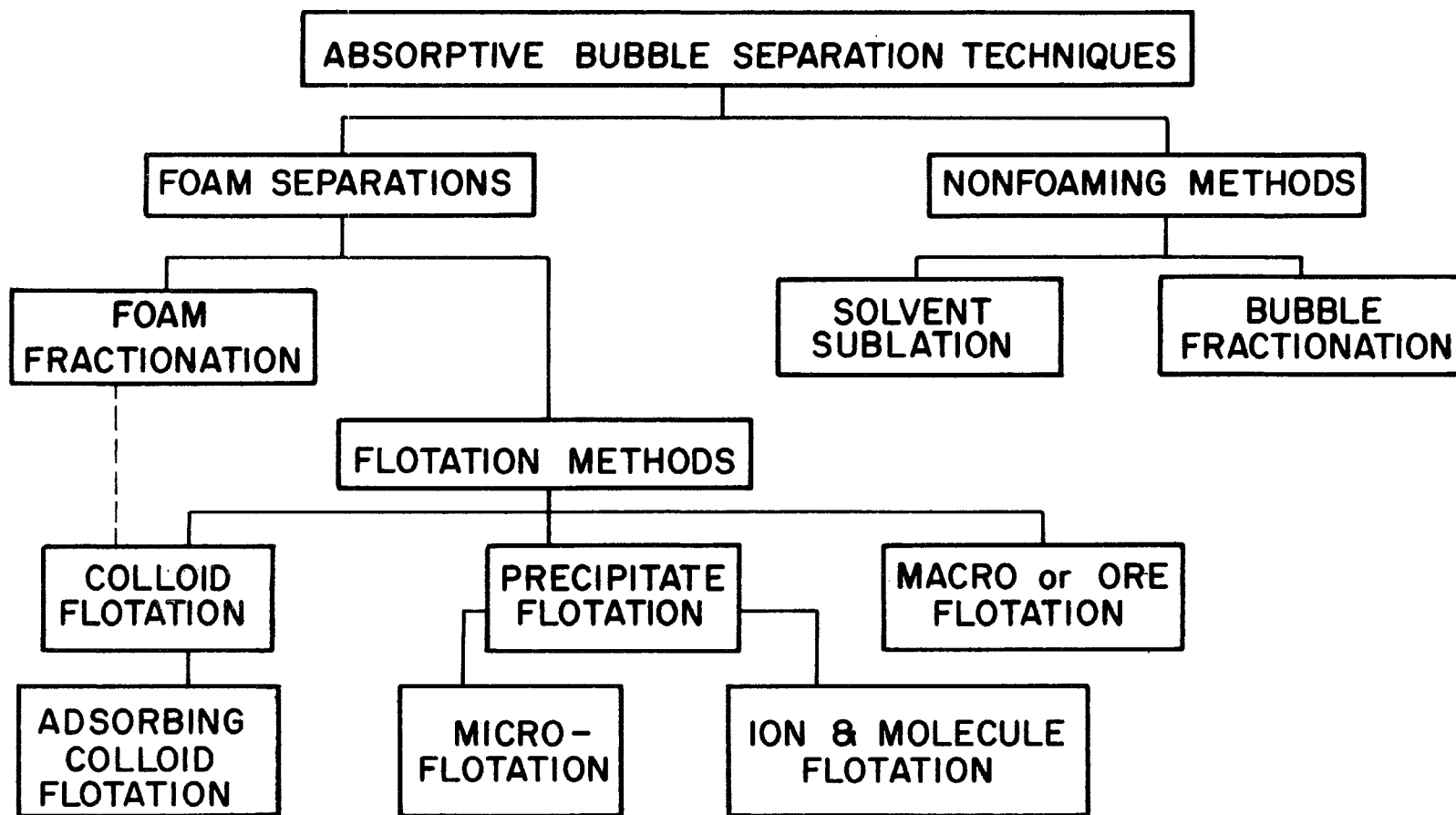


Figure 1. BREAKDOWN OF ADSORPTIVE BUBBLE SEPARATION TECHNIQUES

ment showing the interrelationship of the various processes. Actually, foam separations may be classified in any number of different ways depending on the purpose for which the classification is to be used. Another such scheme is shown in Figure 2 in which the various foam separation techniques are classified according to the relative gas flow rate or degree of surface phase agitation required to effect the separation and the state of subdivision of the substances to be removed prior to the addition of collector. This is a modification of the scheme proposed by Rubin (1968) utilizing a system of nomenclature consistent with current use.

Metals and other surface inactive substances may be removed from dispersion by any of the adsorptive bubble separation techniques. With foam separations the exact mechanistic regime of the transport from the bulk to the surface (foam) phase depends primarily on the state of dispersion or subdivision of the metal both before and after adding the collector surfactant. The sublimate, that is, the surface active product of the interaction between the metal and the collector, may be removed by the mechanisms of flotation or partition. The latter results when soluble sublimes are separated in which case the foam separation is known as foam fractionation. Flotation occurs whenever the components to be removed or its sublimes are insoluble. For one reason or another it is not always possible to distinguish between these two transport mechanisms. This is particularly true for substances of only moderate solubility and with colloidal materials. Although a separate phase is being removed, kinetically the transport may appear to be by partition (and hence the dashed line between foam fractionation and colloid flotation in Figure 1).

The foam separation of metal ions is a foam fractionation process when metal and collector are attracted by simple ion-pair formation or by weak coordination.

		PARTICLE SIZE RANGE		
		MOLECULAR	MICROSCOPIC	MACROSCOPIC
RELATIVE FLOW RATE	HIGH	FOAM FRACTIONATION	COLLOID FLOTATION	ORE FLOTATION
	LOW	ION FLOTATION	MICRO-FLOTATION	PRECIPITATE FLOTATION

Figure 2. CLASSIFICATION OF FOAM SEPARATIONS

In such cases the substrate is soluble and stoichiometric or greater amounts of collector are required. When the metal ion and collector react to form an insoluble product the process is an ion flotation. Again a stoichiometric or greater concentration of surfactant is used and must be added in such a way that it exists as simple ions and not as micelles. Condensation of the metal by pH adjustment or other means prior to the addition of collector results in precipitate flotation. With this process only a very small amount of collector is needed, the lower limit being based on the surfactant requirements for a stable surface (foam) phase. Note that ion flotation is a special case of precipitate flotation, as is microflotation. The mechanism by which the particles are transported from the bulk to the foam phase is identical with all three techniques. The major differences amongst the various foam separation processes and especially these three lie in the nature of the interaction between the collector and the surface inactive substance to be removed.

With hydrolyzable metals, such as aluminum(III), lead(II) and the transition metals, the mechanism, then, depends to a large extent upon the pH of the dispersion medium as well as the nature and concentration of the metal. Other parameters which are very important are the ionic strength and the type and concentration of collector. Additional variables which should be considered in order to understand the controlling mechanisms include temperature and gas flow rate.

Microflotation is a special technique for removing microorganisms and other colloids and is not to be confused with colloid flotation. Individually dispersed colloidal particles are removed by the latter while microflotation is a true flotation process. This is accomplished by enmeshing the ordinarily small particles in the flocculent precipitate of a hydrolyzable metal. Usually the floc is produced by hydroxide preci-

pitiation; aluminum sulfate has been found to very effectively "gather" or "enmesh" organic and inorganic sols over a broad pH range. The resultant floc has the effect of increasing the rate and degree of removal by decreasing the stability of the particles and by increasing their size and providing a new surface for the efficient adsorption of both anionic and cationic collectors. Strongly ionized, soluble collectors may be used since the hydroxide floc stabilizes the surface foam phase. With a stable foam only a very low rate of gas flow is required for rapid clarification. As with precipitate flotation this prevents redispersion of the float and increases the volume reduction by decreasing the amount of bulk liquid transported to the foam. The major advantages of microflotation over conventional settling or foam separation techniques are the high rates of efficient removals possible and low selectivity with regard to the nature of the colloidal particles that are to be removed. As expected, solution pH is the most fundamental parameter controlling the process.

The recent publication of a monograph (Lemlich, 1972) and other excellent reviews in the current literature (Cassidy, 1957; Sebba, 1962; Rubin and Gaden, 1962; Lemlich, 1968; Rubin, 1968; Karger and DeVivo, 1968) obviate the need for such a discussion here. The following sections will present aspects of past and current work by the author on the removal and use of hydrolyzable metals in foam separations. The purpose of the research described in this report was to examine the feasibility of metals removal by foaming, to determine the parameters controlling the process, and to gain an understanding of the mechanisms involved particularly as related to the aqueous reactions of hydrolyzable metals.

EXPERIMENTAL METHODS AND MATERIALS

A schematic of the experimental apparatus used in this work is shown in Figure 3. Nitrogen gas was passed from a cylinder to a foam column through a gas humidifier, glass-wool filter, Manostat rotameter (model FM 1042B) and Moore low-flow-rate controller (model 63 BU-L). 600-ml glass Buchner funnels having a diameter of 10 cm with a fine sintered-glass frit served as the foam columns. Line gas pressure was monitored with an open mercury U-tube manometer and maintained at 30 inches upstream of the controller. Gas flow was adjusted with a fine Nupro needle valve and is reported in a milliliters per minute at average atmospheric pressure and room temperature.

The surfactant collectors were used without special purification and absolute alcohol served as the frother to refine further the small bubbles supplied by the fine frit. The collector solution was prepared with distilled water so that the desired concentration of collector and 1 ml of alcohol could be added simultaneously in a single injection. The collector concentration is expressed as the "collector ratio," S , which is defined as the molar ratio of collector to metal. Solutions of reagent grade sodium hydroxide, sodium perchlorate and nitric or hydrochloric acid were used to adjust the ionic strength and/or pH. Stock solutions of the metals were prepared from the reagent grade nitrate or perchlorate salt. The concentrations remaining after foaming were determined colorimetrically. The details of these analyses and many aspects of the experimental techniques are discussed in the appropriate papers as cited in the text.

Suspensions of the bacterium Bacillus cereus, titanium dioxide, or the clay illite served as the dispersed phases for the colloid flotation and microflotation studies. Suspension turbidities as determined by absorption measurements were used to estimate concentration. Reagent grade aluminum sulfate (alum) was used as the hydrolyzing

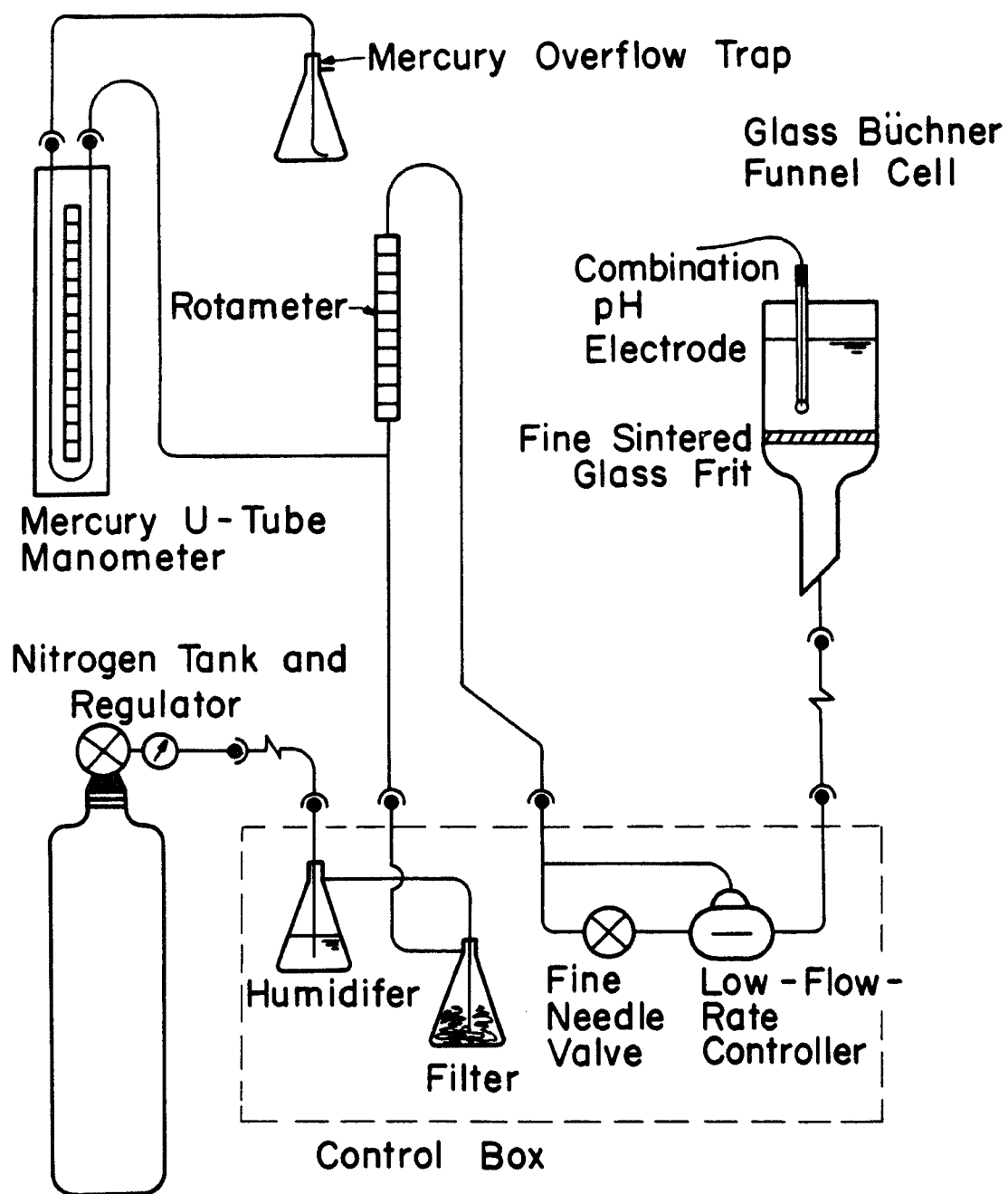


Figure 3 SCHEMATIC OF EXPERIMENTAL APPARATUS

metal coagulant and the applied doses are reported as mg/l of $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$.

Experiments were batch type using 400 ml of the test solution or suspension. After adjustment of the gas flow rate, pH and ionic strength, collector-frother solution was added to the foam column; samples of the bulk were taken at predetermined intervals. The foam phase was undisturbed during experimentation and was not removed for analysis. A pH meter and combination electrode were used to monitor pH during each experiment.

EFFECT OF HYDROGEN ION CONCENTRATION

Hydrolysis and Foam Separation of Lead(II)

When a soluble metal salt is added to water it will dissociate and the ions will become hydrated. In addition, if the metal is capable of undergoing hydrolysis it will also react with water thereby lowering the pH and forming mononuclear and perhaps polynuclear hydroxo species in a stepwise series. The exact distribution of the various species formed, and indeed their nature, will depend primarily on the solution pH, and to a lesser extent on the temperature and the type and concentration of solution components as well as other physical and chemical characteristics of the system. It would be expected then that varying the hydrogen ion concentration of a solution of such a metal would have a profound effect on its removal by foam separation.

A case in point is the effect of pH on the foam separation of lead using the anionic surfactant sodium lauryl sulfate (NaLS) as the collector (Rubin and Lapp, 1969). Typical curves showing the removal of lead(II) as a function of time at collector ratio 2 ($S = 2$) are illustrated in Figure 4. At a gas flow rate of about 25 ml/min the maximum or steady state removals are reached in 20 to 40 minutes at all pH values. As a reminder to the reader these experiments were performed in a short column and the foam phase was

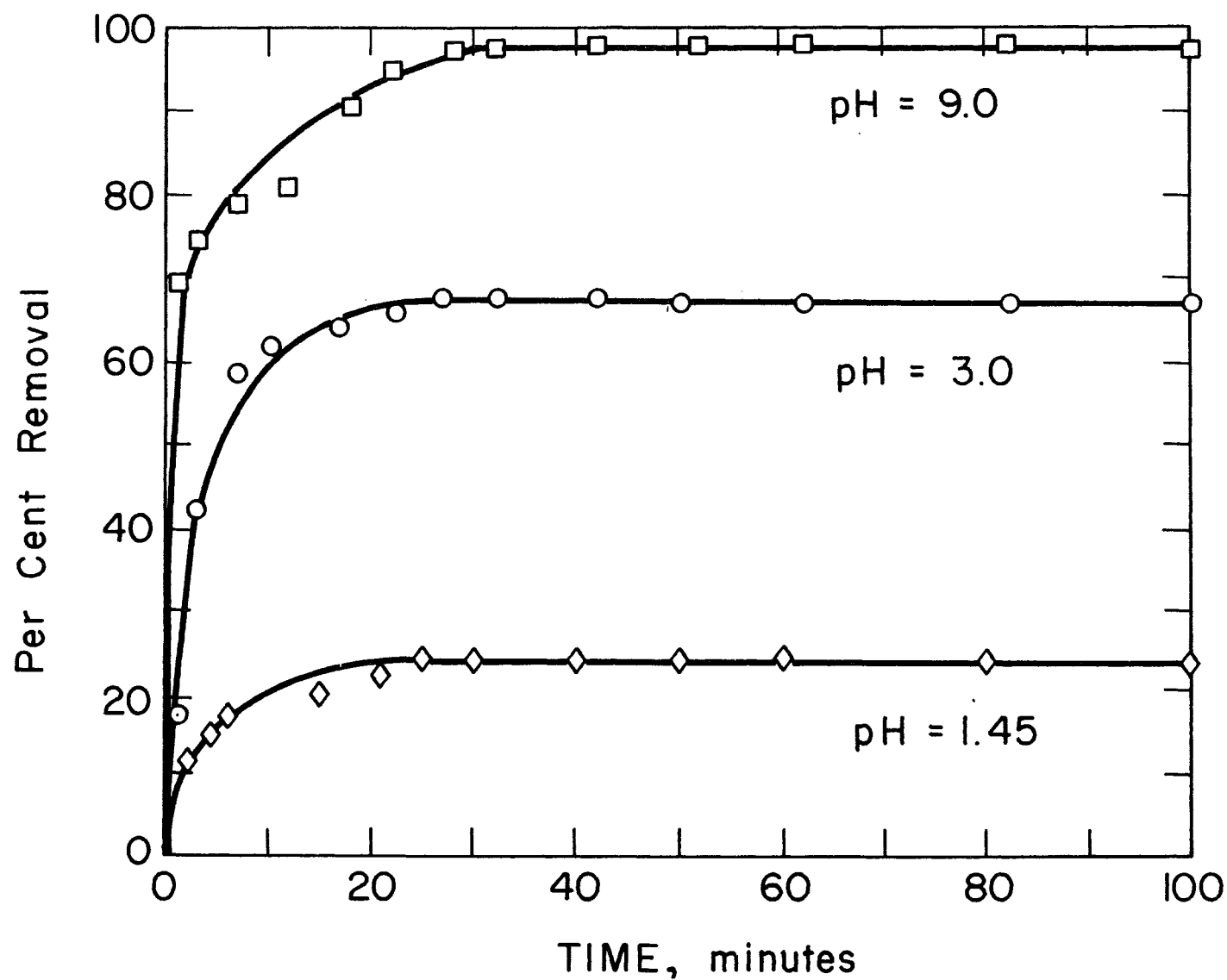
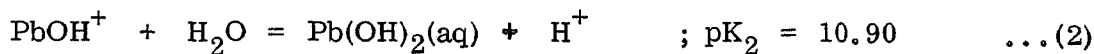


Figure 4 Typical Data for Foam Separation of 0.1 mM Lead(II) as a Function of Time at Different pH. 0.2 mM sodium lauryl sulfate served as the collector.

not removed or recycled during experimentation. Steady state removals are estimated by the 100-minute removals from data such as these. The removal of 0.2 mM lead(II) at minimum ionic strength is summarized in Figure 5 as a function of pH at three collector ratios.

At this concentration of lead there is no evidence of precipitate flotation of insoluble hydroxide at any pH. Note also that the effective pH range of removal increases on the acid side with increasing collector concentration. This range, of course, is characteristic of the particular metal reflecting competition between H^+ and metal ions for collector at low pH and competition between OH^- and collector ions for metal at higher pH. At collector ratios 1 and 2 there is a discrete maximum in removal at pH 8.2. In general, removals were less sensitive to collector concentration at this pH. At the lowest collector concentration there is also an uncharacteristic plateau in removals near pH 5. This plateau was also observed in similar experiments at collector ratio 2 when run at higher ionic strength. Removals decreased as the pH was increased above 10.2, as expected, but were highly scattered and therefore not shown in this figure. This scatter in the results may have been due to the presence of small amounts of the insoluble hydroxide formed by localized precipitation during pH adjustment.

The results in Figure 5 can best be interpreted by examining the hydrolysis of lead(II). The hydrolytic reactions and related equilibrium constants (Fuerstenau and Atak, 1965) are summarized below:



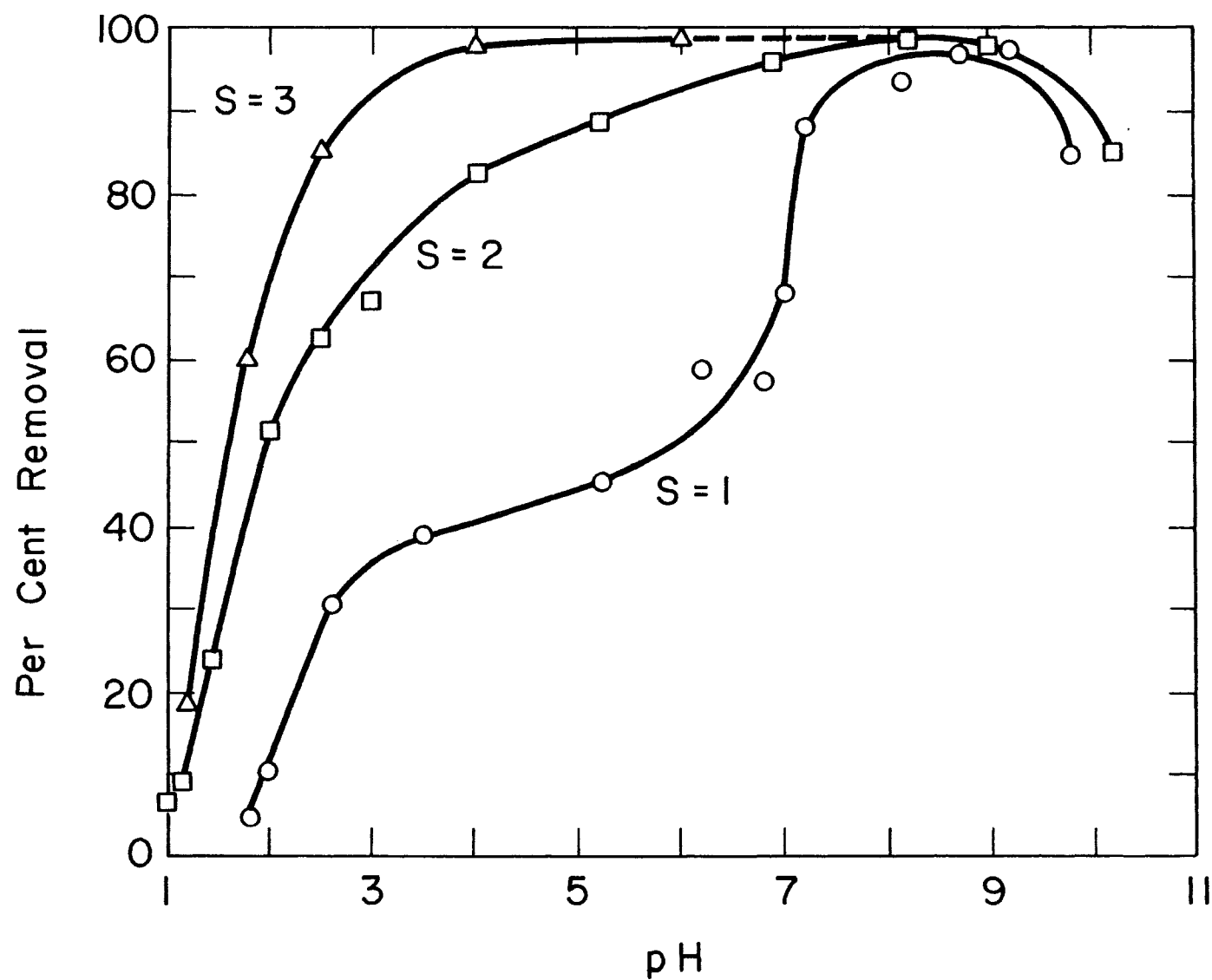


Figure 5 Removal of 0.1 mM Lead(II) as a Function of pH at Different Sodium Lauryl Sulfate Concentrations

For simplicity the waters of hydration are not shown.

In dilute solutions lead hydroxide is soluble:



and therefore precipitate flotation would not be expected in solutions less concentrated than $3.65 \times 10^{-4} \text{ M}$.

The reaction listed above are adequate to define a 10^{-4} M lead(II) solution since at this low concentration the formation of polynuclear species is negligible. A nitrate complex of lead(II) is also known (Gilbert, 1964) but its concentration is negligible in dilute solutions using chloride or perchlorate salts to adjust the pH and ionic strength. Equations 1 through 3 are summarized in Figure 6 which shows the distribution of each species in percent as a function of pH.

Assuming that only positively charged species are foam separated by an anionic collector, the maximum concentration removed in an excess of collector, collector ratio 2 or greater, is given by:

$$M_2 = (\text{Pb}^{2+}) + (\text{PbOH}^+) \quad \dots (5)$$

Similarly, at a collector ratio of 1 the maximum concentration removed is given by:

$$M_1 = 1/2(\text{Pb}^{2+}) + (\text{PbOH}^+) \quad \dots (6)$$

This latter function is indicated in Figure 6 by the dotted line, and explains the plateau in removal at $S = 1$. Increasing the ionic strength also has the effect of reducing the effective collector concentration. This is due to the increased probability of the sodium salt of lauryl sulfate rather than the lead salt being transported to the foam phase.

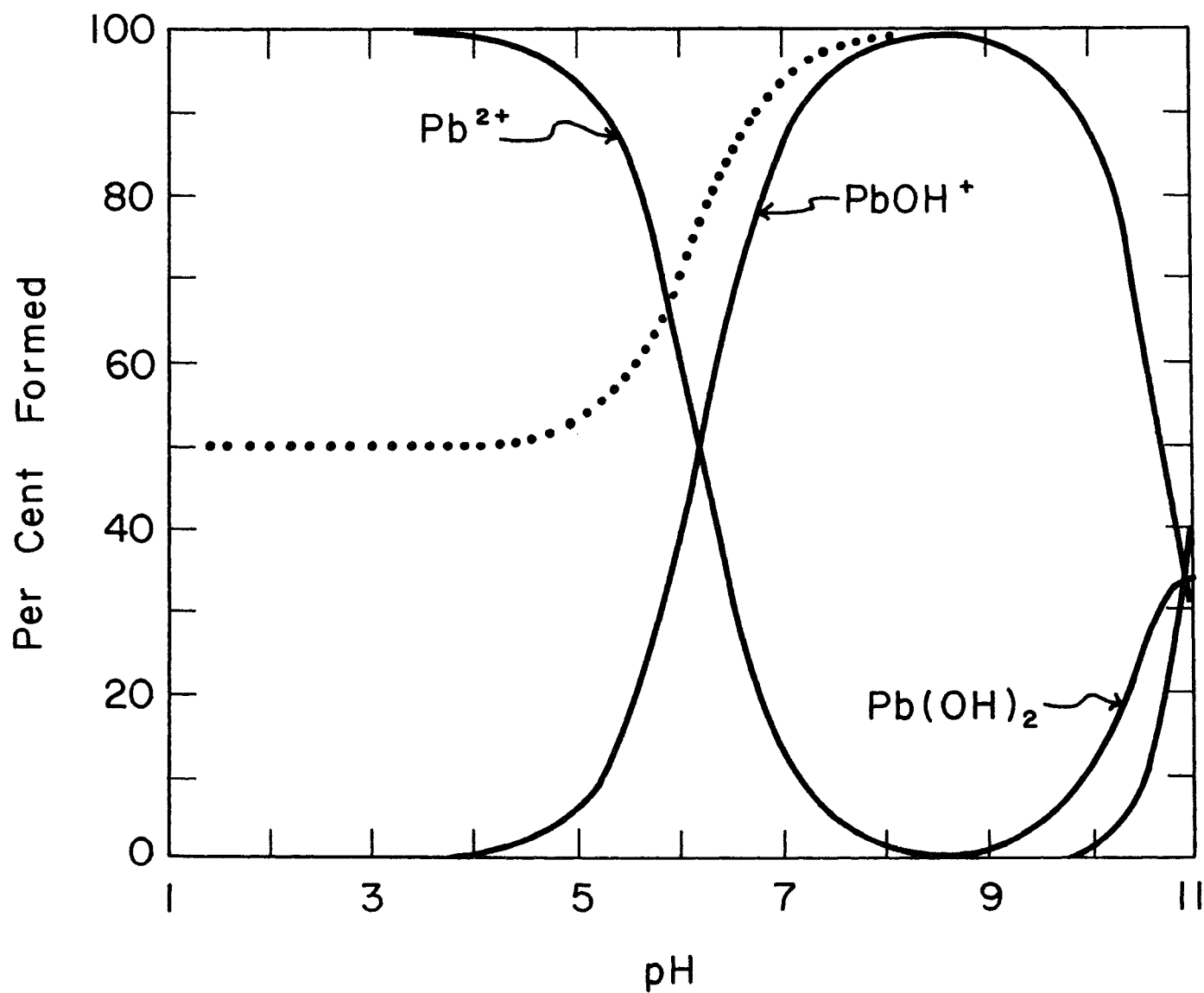


Figure 6 Distribution of Lead(II) Species as a Function of pH. Dotted line is the maximum that can be removed at a collector ratio of unity.

Differences between removals calculated from the above and from the experimental results can be accounted for by H^+ competition at low pH and instability of the lead--lauryl sulfate complex. The removals are less sensitive to collector and reach a maximum at pH 8.2 because stoichiometry of collector to metal is most favorable in the presence of the $PbOH^+$ ion. Removals decrease above pH 8.2 upon formation of soluble lead hydroxide and plumbite ion. It would be expected that the latter would be removed by a cationic collector.

In summary, the results demonstrate the applicability of hydrolysis data to estimating removals by foam separations. Such data alone, however, are not sufficient to completely characterize the system. Other factors which must be considered include the stability of the metal--collector complex, the type of collector used, and the effect of competing cations. Before examining some of these and other variables it would be instructive to consider the effect of pH on the foam separation of a metal in which its hydroxide is insoluble and the success of hydrolysis data to predicting flotation.

Precipitate Flotation of Iron(III) and Zinc(II)

Iron(III) and zinc(II) also hydrolyze in solution but unlike lead form insoluble hydroxides in the ca. 10^{-4} M concentration range. If it were assumed that these hydroxide precipitates would be completely removed from dispersion, say by precipitate flotation, then a "theoretical" precipitate flotation curve could be drawn based on calculation from hydrolysis data (Rubin and Johnson, 1967; Rubin and Lapp, 1970). For iron(III) at room temperature, neglecting polynuclear species, the distribution of soluble iron species, C_a , is given by:

$$C_a = (Fe^{3+}) + (FeOH^{2+}) + (Fe(OH)_2^+) + (Fe(OH)_4^-) \quad \dots(7)$$

or as a function of pH in acid solution:

$$C_a = K_s H^3 + K_s K_1 H^2 + K_s K_1 K_2 H \quad \dots(8)$$

where K_s is the dissociation or "solubility" constant, $(Fe^{3+})/(H^+)^3$, K_1 and K_2 are the first and second hydrolysis constants for iron(III), respectively, and H is the hydrogen ion concentration (activity) calculated directly from pH measurements. Assuming 100% efficiency the percent removal of the metal precipitate is calculated by substituting C_a into $\%R = 100(1 - C_a/C_o)$, where C_o is the total (analytical) concentration of iron added. Such a curve compared to experimental data is shown in Figure 7. Further details about its derivation are given elsewhere (Rubin, 1968).

The calculated precipitate formation curve for 0.2 mM iron(III) predicts that the metal is completely soluble up to pH 2.67 (the precipitation point). At the precipitation point and above ferric ions at this concentration exist in both soluble and insoluble forms. However, at pH 4 only an insignificant fraction of the metal remains in solution. The removals shown in Figure 7 at C mM concentration of NaLS and gas flow rates of G ml/min. fall on the curve or to its left. The removals at pH values less than pH 2.67 must be due to the foam separation of dissolved iron(III) species. Removals on the curve, then, are due to precipitate flotation, while removals between the curve and the precipitation point are due both to ion removal and precipitate flotation. The removals at the higher collector concentrations and gas flow rates increase with pH. At the lowest gas-rates and NaLS concentrations the removals are lower but increase sharply at pH values at and above the precipitation point in excellent agreement with the calculated curve.

The results, that is, the pattern of removal with pH is similar for both iron(III) and aluminum(III) (Rubin, unpublished). Both of these metals form polynuclear ions in dilute solution. Since no one soluble species predominates below the precipitation point the removal curves do not demonstrate a plateau in removal as found for the lead

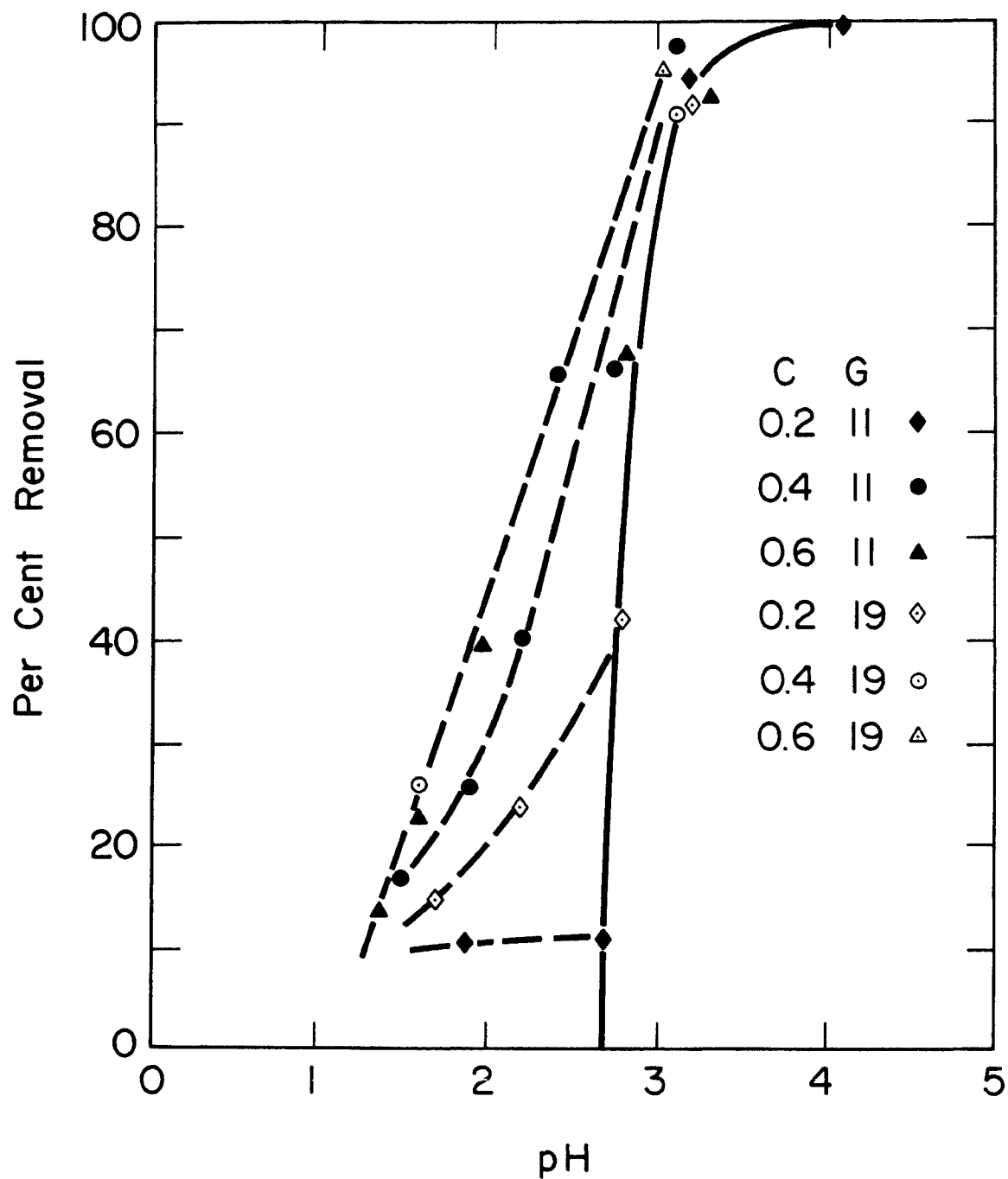


Figure 7 Removal of 0.2 mM Iron(III) as a Function of pH at Different Gas Flow Rates G (ml/min) and Concentrations C (mM) of Sodium Lauryl Sulfate. Solid line is the calculated precipitate flotation removal curve.

system. Examination of the hydrolytic reactions of zinc(II) (Kanzelmeyer, 1961), on the other hand, reveals that the free unhydrolyzed Zn^{2+} ion is the species in greatest concentration up to a pH of about 8; ZnOH^+ is formed but is almost completely negligible in concentration. Also at the concentration examined, 0.1 mM zinc(II), there was no evidence of soluble polynuclears. Above pH 8.5 and below pH 11 the insoluble hydroxide is predominant with soluble Zn(OH)_2 molecules making up much less than 3 percent of the total. Thus, the total concentration of soluble zinc is given by:

$$C_a = (\text{Zn}^{2+}) + (\text{Zn(OH)}_2) \quad \dots (9)$$

The predicted precipitate removal curve is compared with experimental data in Figure 8 showing the removal of 0.1 mM zinc(II) with various concentrations of NaLS at a gas flow rate of about 25 ml/min.

The removals are greatest, even at very low collector concentrations, in the pH region of hydroxide precipitation. Agreement between calculated and observed removals at the lower pH limit of hydroxide formation is excellent. Removal above pH 10 decreases upon formation of negatively charged zinc species; however, this occurs at a lower pH than predicted by the solubility limits of the precipitate on its basic side. There is the possibility that the precipitate has acquired a negative charge at the higher pH due to adsorption of hydroxide ions and thus has a lowered affinity for the collector.

Although the removals are relatively insensitive to collector concentration above pH 8, at lower pH the removal of Zn^{2+} is quite dependent upon this parameter. At a stoichiometric collector ratio ($S = 2$) the removals averaged about 92% between the pH range of 3 to 8 forming a plateau in the removal curve. This plateau is indicative of a single predominant ionic species. The difference between the observed removal and

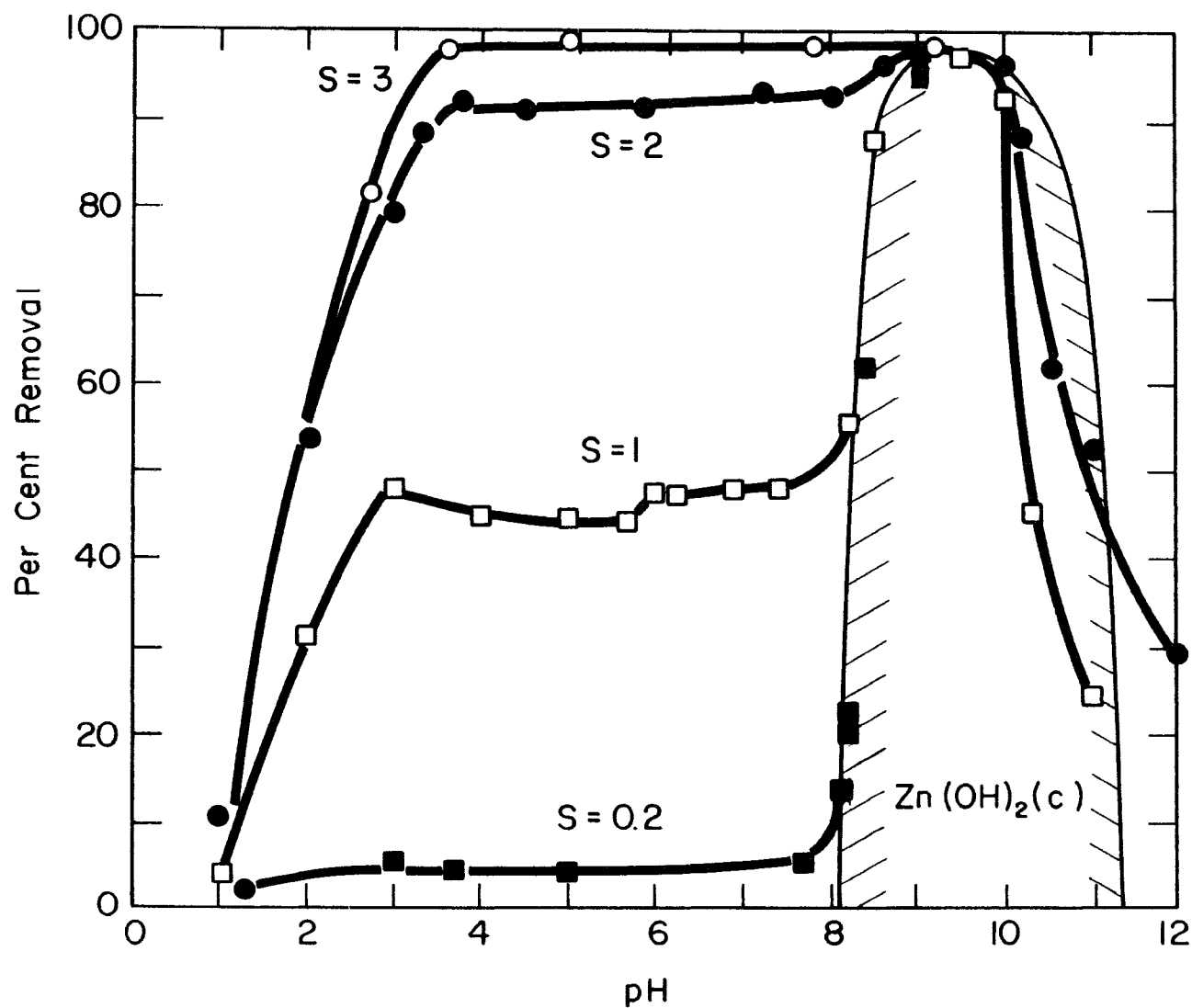


Figure 8 Removal of 0.1 mM Zinc(II) with Sodium Lauryl Sulfate as a Function of pH. Experimental results are compared with calculated precipitate flotation curve.

the theoretical of 100% is due to the instability of the zinc--lauryl sulfate complex.

Below pH 3 removals drop off sharply because of protonation of the collector.

Studies on the Foam Separation of Copper(II)

Soluble and condensed copper(II) are also efficiently removed by foam separation with NaLS. The removal pattern with pH is similar in many respects to those for zinc and lead. Unlike iron and lead, which readily coordinate with oxygen atoms, there is very little interaction between copper and lauryl sulfate. The substrate is completely soluble and thus the mechanism under which copper is removed at low pH is unambiguously a foam fractionation. For these reasons copper(II) is ideal for comparing the various metals and collectors as well as offering a simple comparison between partition and flotation processes by merely changing pH (Rubin, Johnson and Lamb, 1966).

In practice, of course, foam fractionation requires tall columns with provisions for reflux and foam drainage to maximize the separation and to reduce the amount of liquid carried over with the foam. For the studies outlined here, a short column was used since this is experimentally convenient and permits the controlling variables to be studied individually and independently of one another. During experimentation the foam phase was not disrupted and only a single experiment was performed on each single batch.

COMPARISON OF ION AND PRECIPITATE REMOVAL

Interactions Between Solution Components

The nature of the collector surfactant is very important. Figure 7 suggests that NaLS, a strongly ionized anionic surfactant, is capable of removing dissolved, colloidal, and condensed iron(III). Soluble ferric species, except at high pH, are positively charged and therefore their removal from solution by a cationic collector would not be expected.

Iron precipitates, however, are known to be floated by amine collectors. These effects, the non-removal of soluble iron and the floatability of its hydroxide precipitate using stearylamine as the collector are shown in Figure 9. This surfactant is a weakly basic primary amine being positively charged only in acid solutions. Iron is not removed by the amine until the precipitation point and at higher pH the removals are less than predicted. The scattered and non-reproducible results shown in this figure are due to the variable character of iron hydroxide and because iron and stearylamine form an unstable complex. Contrast this to the removal of copper by the same amine as shown in Figure 10. The removals form a smooth curve and approach 100 percent because copper is a strong nitrogen coordinator and interacts strongly with amines. Because of this its ions although positively charged are also partially removed.

It is apparent that the removal of hydrolyzable metals in soluble systems involves a competition between collector and the various ions in solution. Where coordination between collector and the metal is a minimum electrostatic effects predominate. In these cases the substrate is soluble and removals are sensitive to the other components of the solution such as sodium and other simple ions. This is the "ionic strength" effect and is illustrated in Figure 10 for copper(II) and in Figure 11 for zinc(II), both using sodium lauryl sulfate as the collector. The ionic strengths were adjusted with sodium perchlorate.

Removals of 0.3mM copper(II) after foaming for 40 minutes are shown as a function of pH at different ionic strengths, all other conditions being held constant. Points on the extreme left in Figure 10 are for removals at the lowest pH possible at each ionic strength. Shown also in this figure is a single point on the precipitate flotation curve at an intermediate ionic strength. That zinc removal is similarly

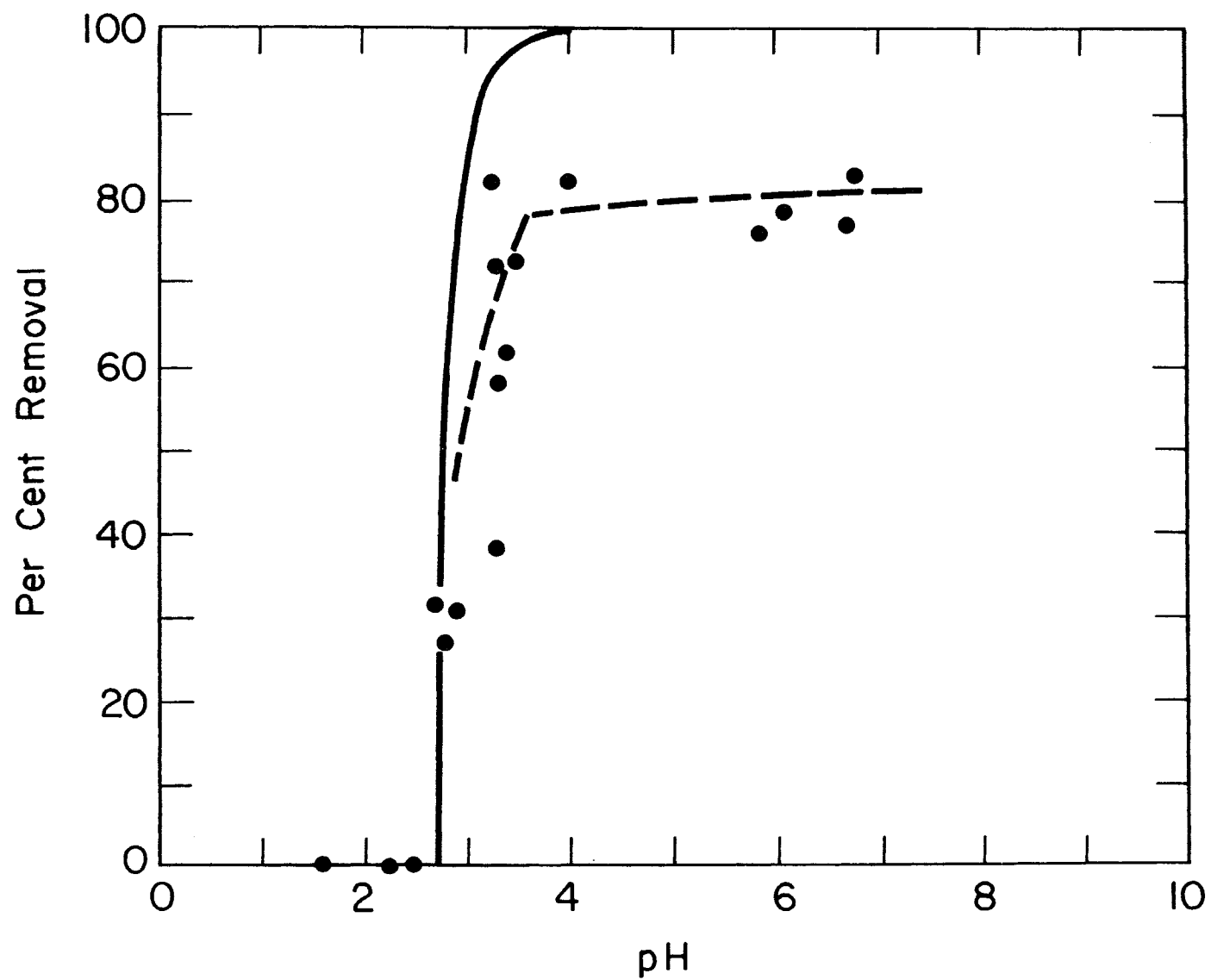


Figure 9 Removal of 0.2 mM Iron(III) with Stearylamine as a Function of pH. Experimental results are compared with calculated precipitate flotation curve.

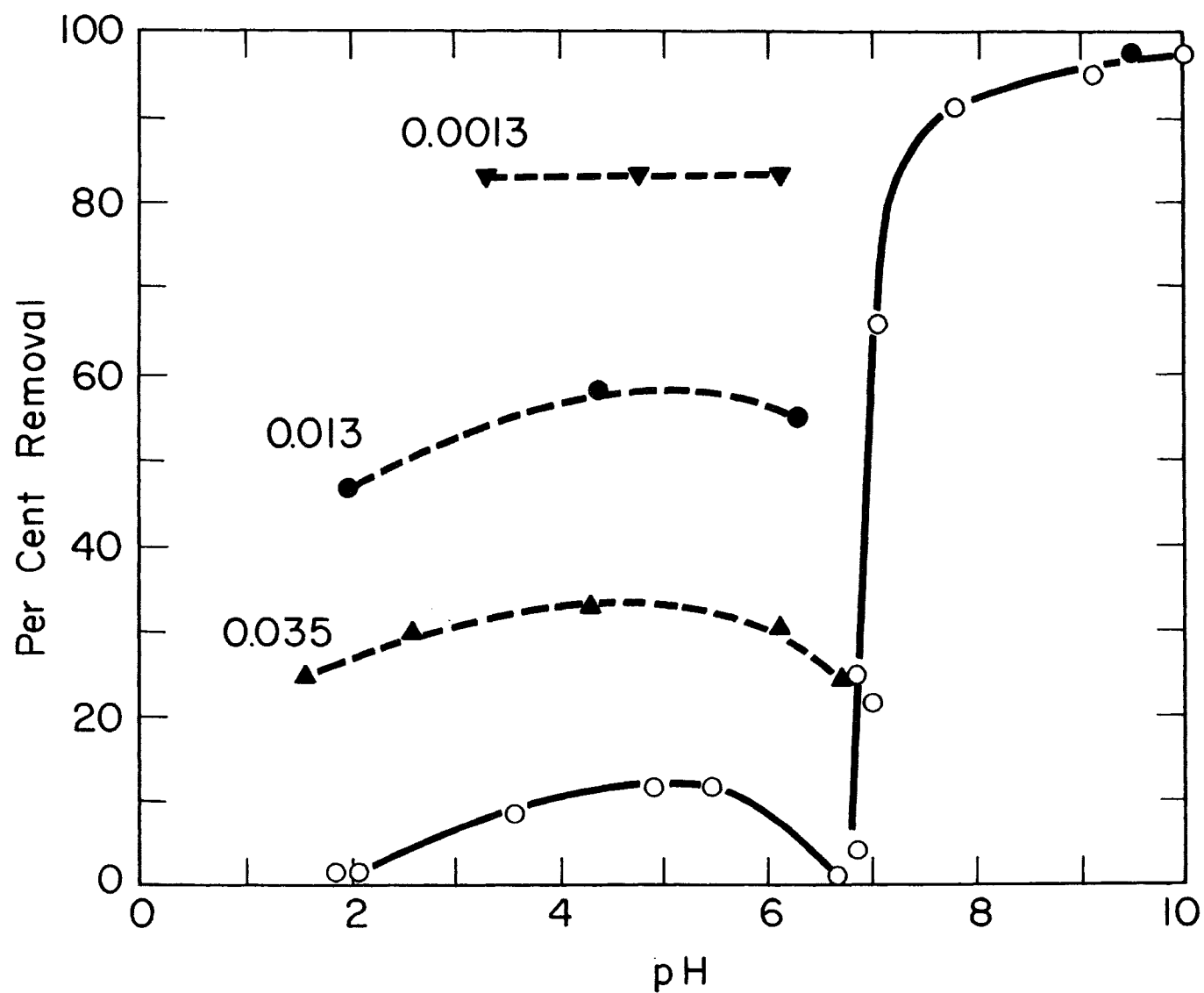


Figure 10 Foam Separation of 0.3 mM Copper(II) with Stearylamine (open points and solid line) and NaLS at Different Ionic Strengths (blackened points and dashed line). Removals as a function of pH.

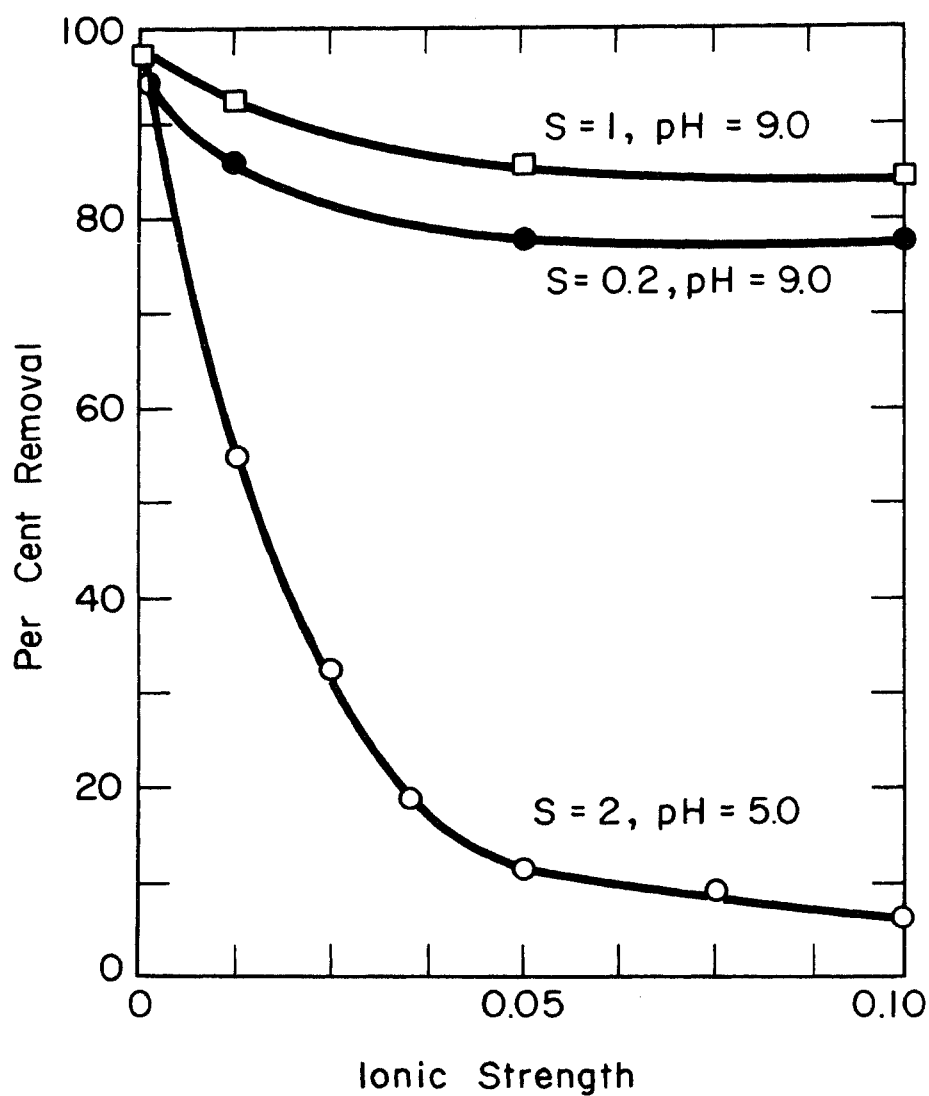


Figure 11 Effect of Ionic Strength on the Foam Separation of 0.1 mM Zinc(II) with Sodium Lauryl Sulfate.

affected is shown in Figure 11. Experiments were conducted at pH 5 where the Zn^{2+} ion predominates and at pH 9 where essentially all of the metal is present as the precipitate. These figures demonstrate a fundamental difference between precipitate flotation and the foam fractionation of metal ions. Thus, although there may be a special affinity between collector and hydrolyzable metal the probability of surfactant entering the foam as an ion-pair with a neutral salt increases with an increase in the concentration of the latter. On the other hand, precipitate removal is non-stoichiometric and surfactant need only react with ions on the surface of the condensed phase to effect its removal. This requires very small amounts of the collector, the excess being used to stabilize the surface phase.

Differences in ion and precipitate removal with regard to surfactant requirements will be examined further in the next section. In addition to altering the ionic competition in a system, reductions in removals with increasing ionic strength may be attributable in part to decreases in activity of the soluble species. The salt content of the solution may also influence removals by changing the critical micelle concentration of the collector and by altering foam stability. Note then that selectivity in some foam separation systems could be improved by adjusting the concentration of neutral salts as well as the pH.

Effect of Metal and Collector Concentrations

To a large extent the effects of collector concentration on both ion and precipitate removal are shown in Figures 5, 7, and 8. As indicated by these figures and in Figure 12 for 0.3mM copper (II) at pH 6.3 (Rubin, Johnson and Lamb, 1966), ion removal is strongly dependent on collector concentration requiring stoichiometric or greater concentrations for complete removal. That precipitate flotation is considerably less affected is demonstrated in Figure 13 for the same concentration of copper at pH 9.5. Neither

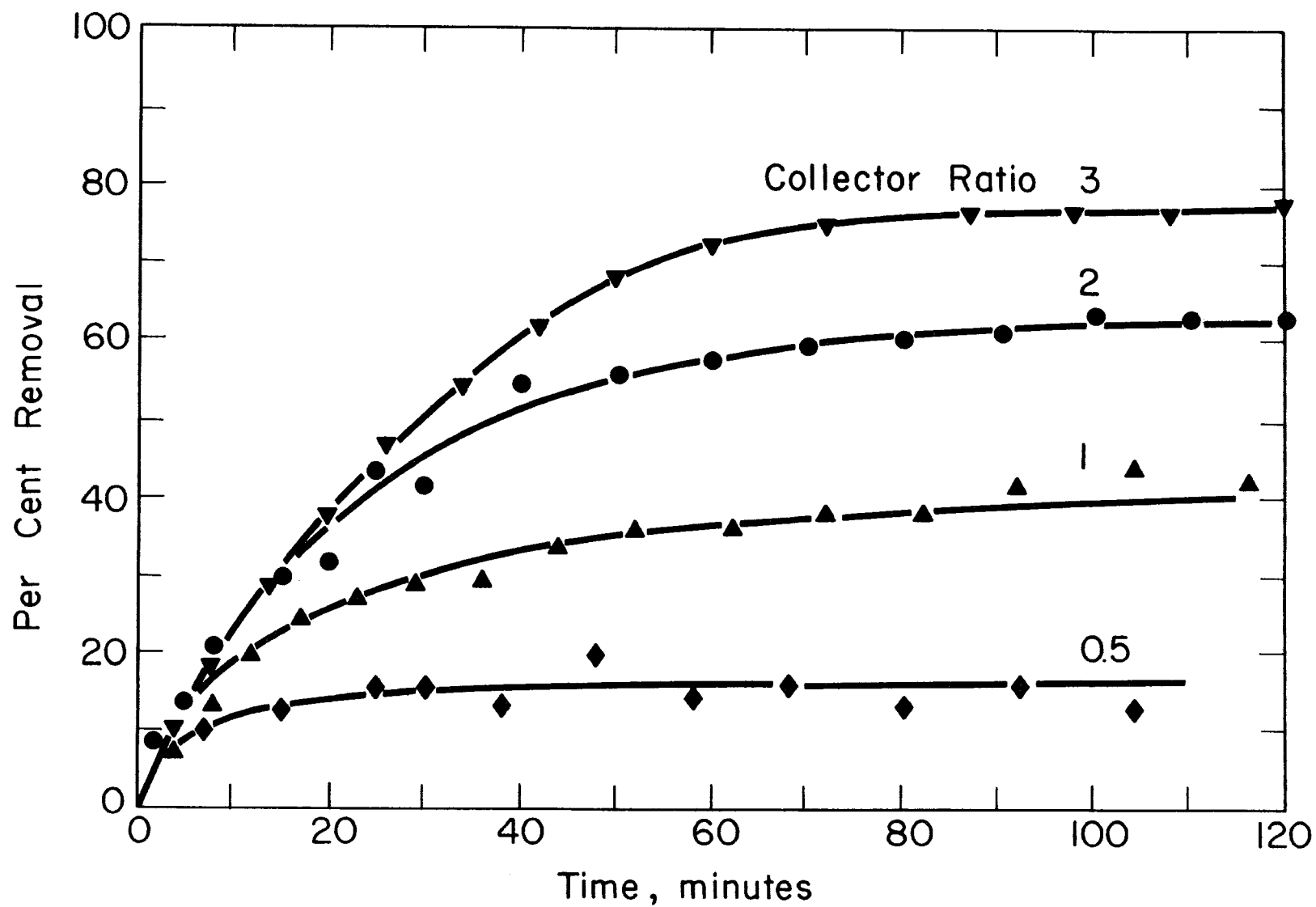


Figure 12 Effect of NaLS Concentration on the Foam Fractionation of 0.3 mM Copper(II). Ionic Strength 0.013 at pH 6.3.

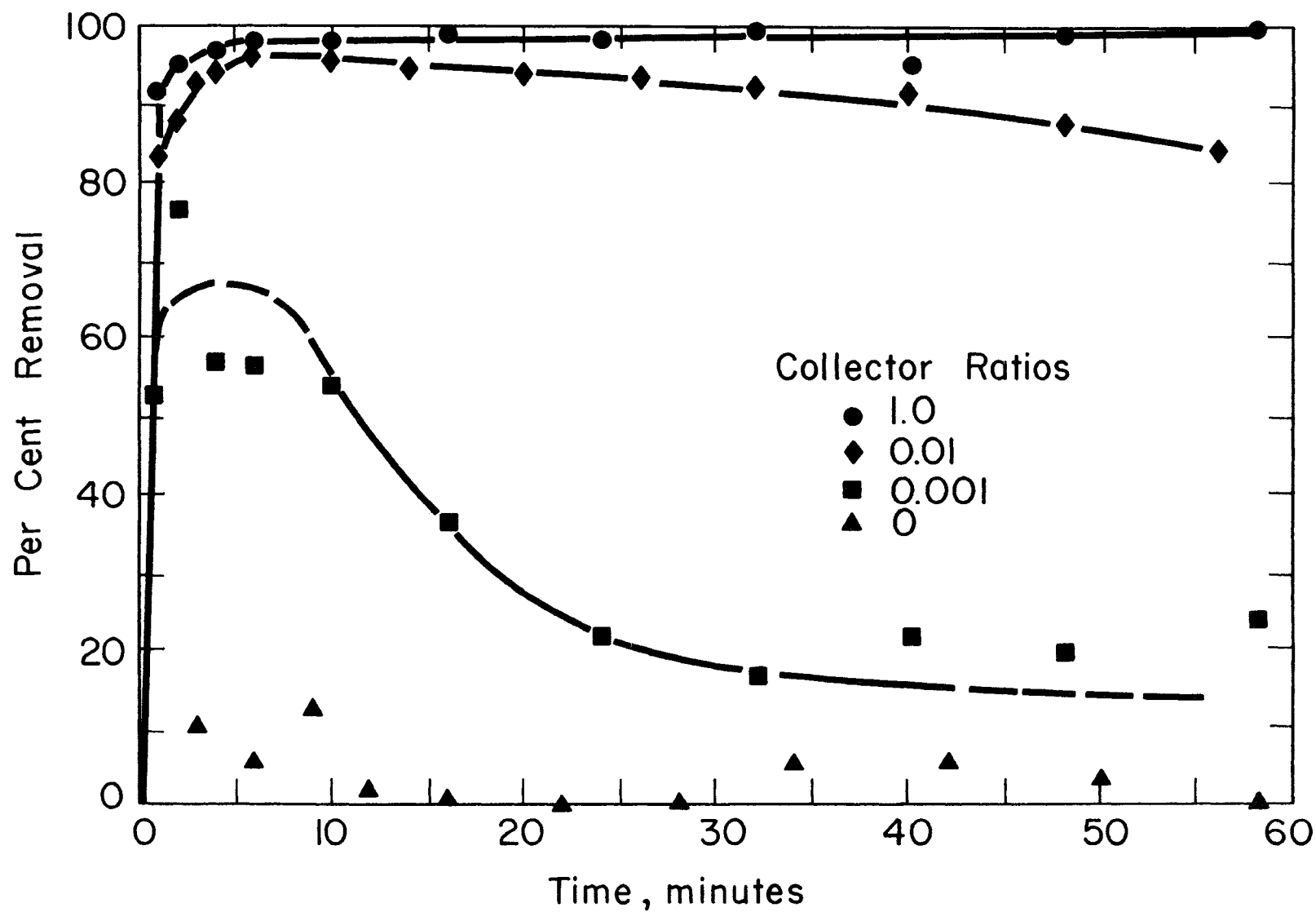


Figure 13 Effect of NaLS Concentration on the Precipitate Flotation of 0.3 mM Copper(II). Ionic Strength 0.013 at pH 9.5.

the rate nor the total removal of copper hydroxide is affected at collector ratios of 0.2 or greater. At very low amounts of surfactant the rate of removal is still high but the surface phase is unstable and after a few minutes of foaming the float is re-dispersed and removals decrease correspondingly. This effect is evident when using alcohol frother but without collector as shown in the lower portion of Figure 13. Partial removal of the precipitate is observed since ethanol has some surface active properties, however, without collector redispersion occurs very rapidly.

Since ion removal is strongly dependent upon stoichiometry of collector to metal an increase in the concentration of the latter would require a corresponding increase in surfactant. The amount removed at steady state is dependent only on the collector ratio, however, the rate is altered by the metal concentration. Conversely, neither the rate nor degree of precipitate flotation is affected by the initial concentration of the metal provided enough surfactant remains after reaction with the surface of the condensed phase to produce a stable foam.

Effect of Temperature and Gas Flow Rate

Two parameters that might be important in foam separation are temperature and gas flow rate. Both are important considerations not only in the way in which they might affect removals but also in what they tell us about the mechanisms of the process. In general, for example, temperature has been found to have very little affect (Rubin, Johnson and Lamb, 1966; Schoen and Mazella, 1961) provided foam structure is not destroyed thermally. Therefore, it is apparent that foam separations of metal ions are not controlled by such temperature sensitive parameters as diffusion and surface tension.

Gas flow rate, on the other hand, as shown in Figure 14, strongly affects the rate of removal of soluble sublates without significantly affecting the steady state removals.

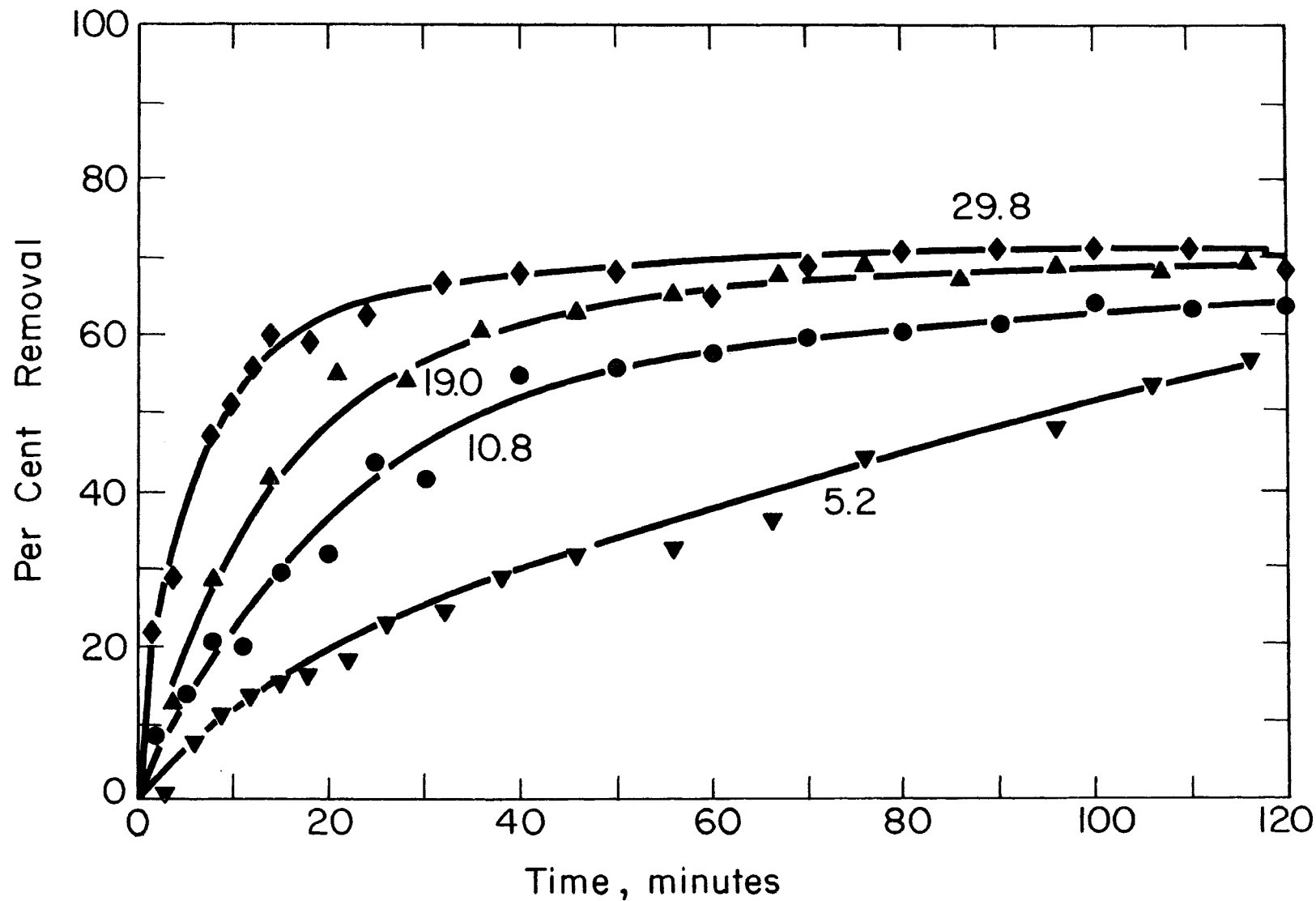


Figure 14 Effect of Gas Flow Rate on the Foam Fractionation of 0.3 mM Copper(II) with 0.6 mM NaLS. Ionic strength 0.013 at pH 6.3.

The effect is not as great with insoluble systems, apparently the larger the particle being removed the less the rate of removal is determined by gas flow rate. The difference between ion and precipitate removal is reflected in these observations. The removal of soluble sublates involves their distribution or partition between gas and aqueous phases. The greater the interfacial area as occurs with increasing gas rate the greater the removal at any given time although the total removal depends upon stoichiometric relationships. Precipitates on the other hand are levitated out with bubbles that serve to reduce the effective density of the particles. Interfacial area is not as important and the process is not controlled by adsorption at the bubble surface. In fact, because gelatinous precipitates are easily broken up and once redispersed in the bulk are extremely hard to refloat in increased gas rate may be detrimental to precipitate and microflotation. A further disadvantage of high gas rates, especially with soluble systems, is that the amount of bulk liquid entrained in the foam may be very high resulting in a smaller volume reduction.

MICROFLOTATION FOR THE REMOVAL OF COLLOIDS

Studies with the Bacterium *Bacillus cereus*

When individual colloiddally dispersed particles are removed by foaming the exact mechanistic regime of the process may be ambiguous appearing to operate by partition. Generally, the rate of removal is rather slow and the particles may be selectively removed. Unless a chromatographic separation is desired the process would be more rapid and less selective if the particles were increased in size and if a new surface was produced for the efficient adsorption of collector. Both are accomplished by the addition of hydrolyzing metal and pH control prior to foaming. The resultant process

is known as "microflotation." Microflotation was developed as a consequence of the author's work with hydrolyzable metals (Rubin and Cassell, 1965) and has now been applied to both organic and inorganic colloids.

Applications and the effects of several parameters on the process have been described in detail elsewhere (e.g., Rubin, et al., 1966). In general, microflotation is sensitive to the same variables as precipitate flotation. What is unique is the use of a hydrolyzing metal to aid in the removal of sols. This aspect will be discussed here.

The first example is the microflotation of the gram positive bacterium Bacillus cereus (Rubin and Lackey, 1968). Removals of the organism within 20 minutes of foaming using lauric acid as the collector are shown in Figure 15. Without aluminum sulfate (alum) the removals are irregular; high removals occur only in acid solutions. Even with this poor collector the addition of alum results in rapid and essentially complete separation near pH 7. Flotation of the organism has also been examined without collector or frother both with and without alum. There was no removal at any pH. Aggregation alone does not result in flotation when collector and frother are not used.

That removal in such systems is a combination of colloid flotation of free particles and precipitate flotation of sol trapped in an alum floc is demonstrated in Figure 16, which shows removals by foaming with NaLS and by settling after adding alum. Bacterial cells are removed at pH 4.5 and below when alum is not used. This is a pH unit less than observed with lauric acid, however, the removals with NaLS are greater and form a smooth curve. At low pH the organisms are coagulated by hydrogen ion, that is, their negative charges are reduced so that an anionic collector is adsorbed. Lauric acid, on

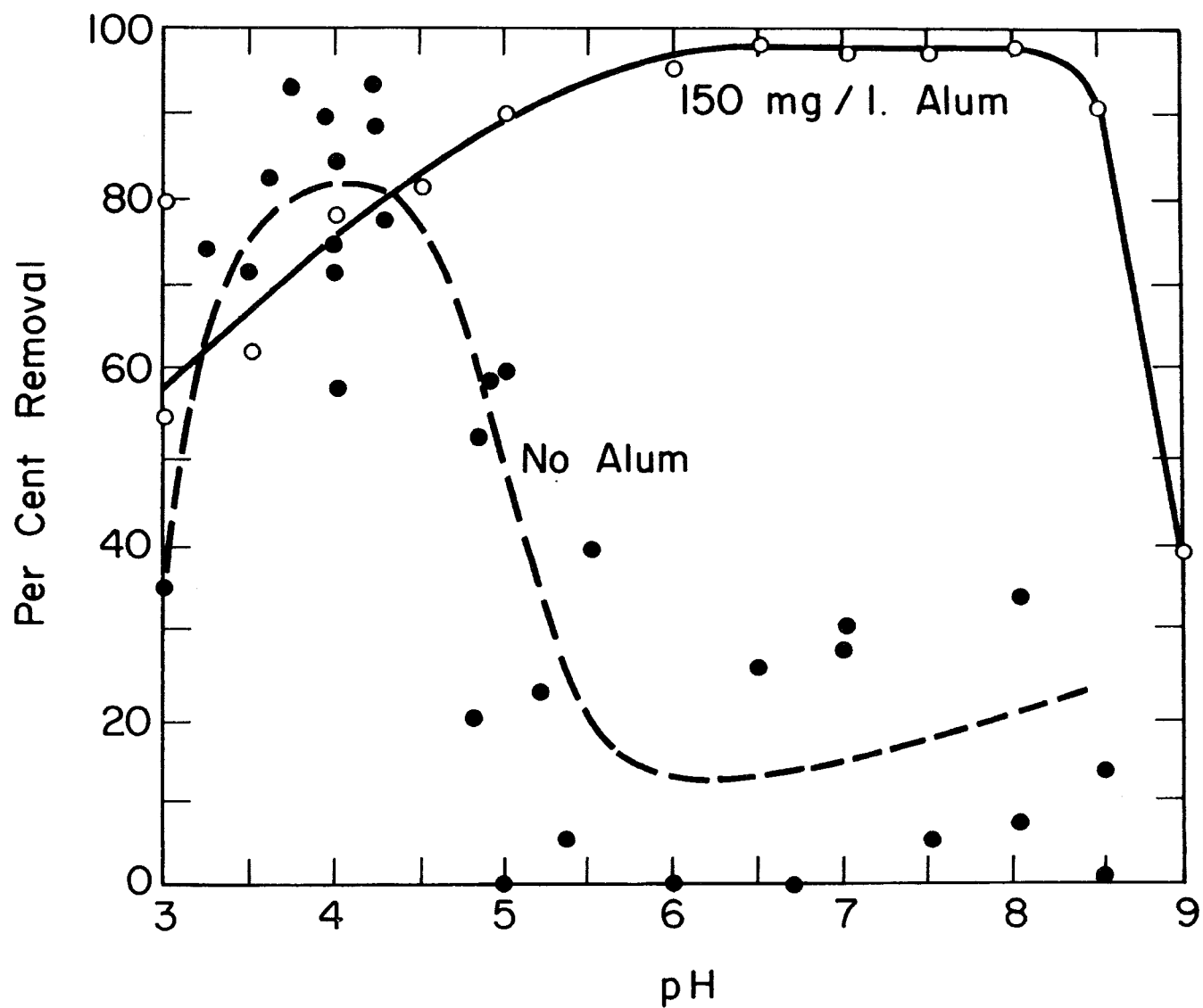


Figure 15 Foam Separation of *B. cereus* with and without the Presence of Aluminum Sulfate using Lauric Acid as the Collector. This compares microflotation with colloid flotation.

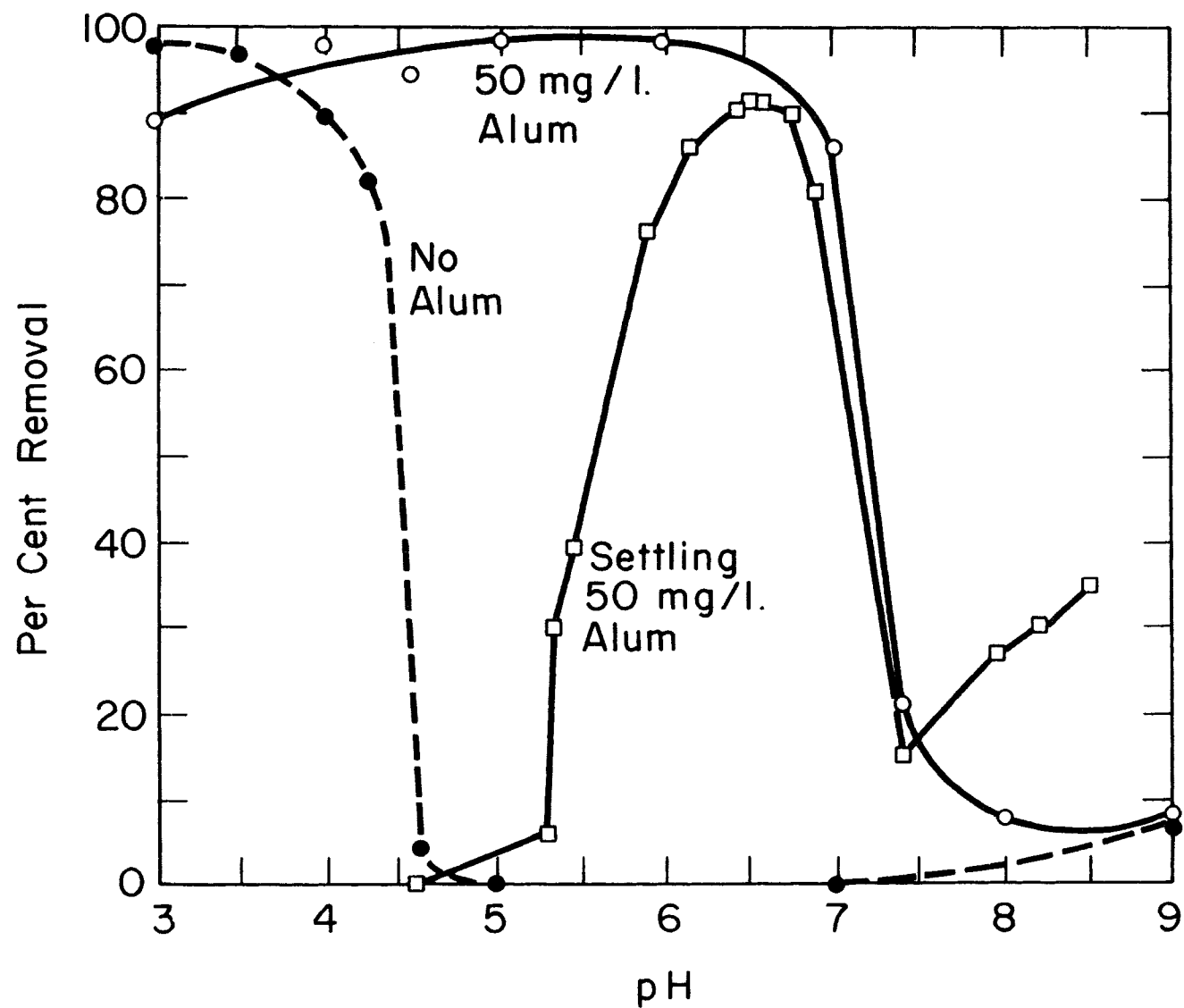


Figure 16 Removal of *B. cereus* with NaLS, comparing Colloid Flotation and Settling with Microflotation.

the other hand, is uncharged in acid solution and is thus capable of hydrogen bonding with the cell surfaces at slightly higher pH. In the pH range between 5 and 7 the cells can be removed from dispersion in the presence of alum by settling or flotation. This is the "sweep zone" of aluminum hydroxide precipitation and enmeshment of the organisms in the resultant floc (Rubin and Hanna, 1968). Note that the ability of the organisms to be collected is sharply reduced once the optimum pH is exceeded. At this boundary the hydroxide floc goes back into solution as the negatively charged ion, $\text{Al}(\text{OH})_4^-$.

Other microorganisms successfully removed from aqueous dispersion include two species of algae and E. coli (Rubin, et al., 1966) and A. aerogenes (Rubin, 1968).

Studies With the Clay Illite

Microflotation was originally introduced as a removal technique for microorganisms and other organic sols. Recently it has been demonstrated that the process is just as effective with inorganic systems and that removal is subject to the same variables. An example is the flotation of the clay illite (Rubin and Erickson, 1970).

Figure 17 shows the removals of illite obtained at 16 minutes as a function of pH using about 30 mg/l NaLS. As with B. cereus the clay is removed only at low pH when alum is not used. Upon adding the flocculating agent the pH range of removal is widened with increasing concentration. As demonstrated in Figure 18 the addition of alum also increases the rate of clarification; this occurs in the pH regions of aluminum hydroxide precipitation. Here the sols are enmeshed, or gathered, in the flocculent precipitate and the floc itself provides the sites for the adsorption of collector. In general, because the hydroxide is formed over a wider pH range with increasing metal concentration the pH range of removal also increases on the alkaline side. The pH range of removal for many sols in acid solutions is independent of the alum concentration and the rates of

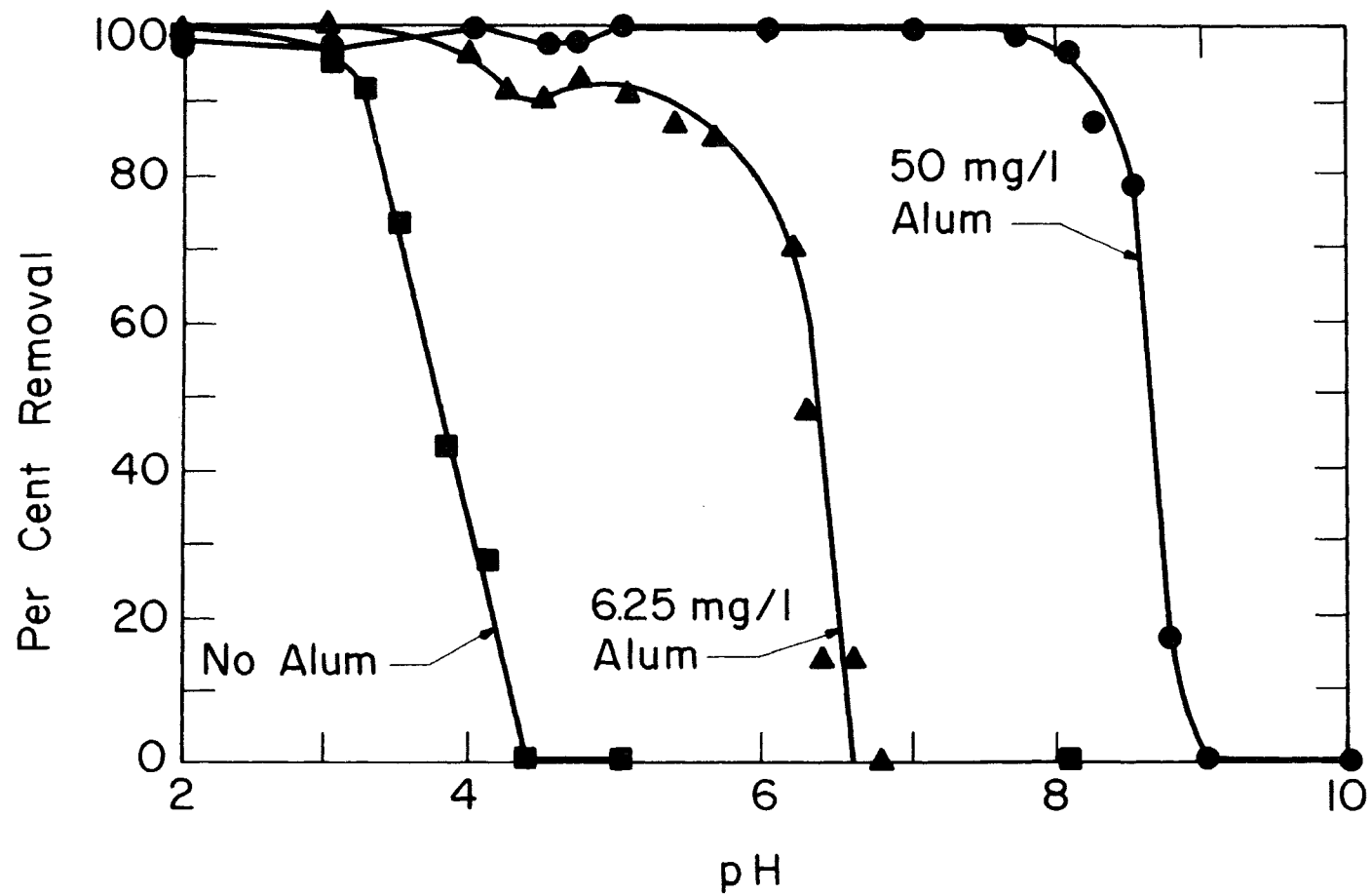


Figure 17 Effect of Aluminum Sulfate Concentration on the Foam Separation of Illite with Sodium Lauryl Sulfate.

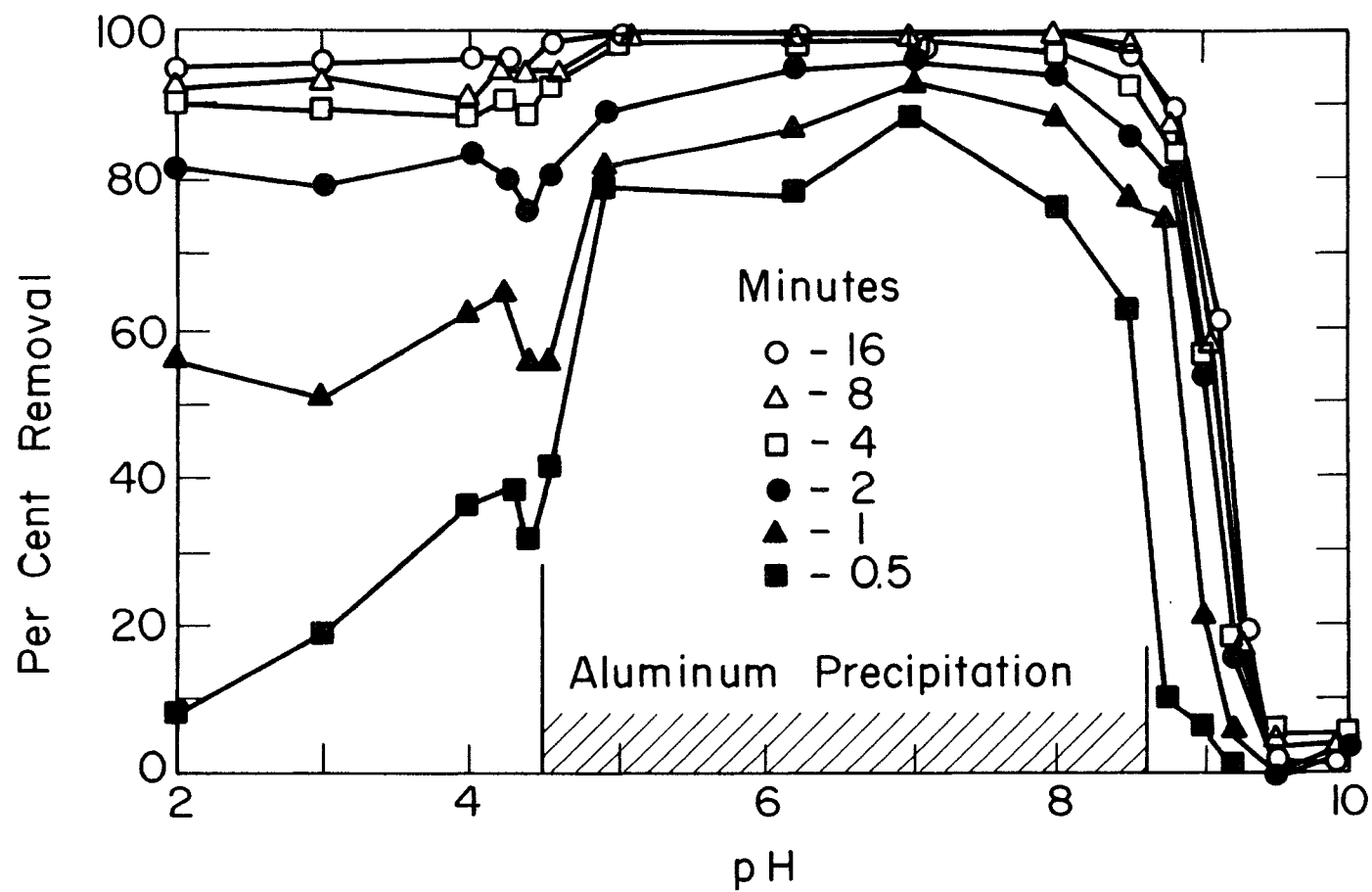


Figure 18 Effect of pH on the Rate of Illite Removal using 100 mg/l Alum and 30 mg/l NaLS. Removals at a given time are shown and the range of aluminum hydroxide precipitation is defined.

removal are considerably less. Changes in collector concentration also do not significantly affect the removal rate.

In summary, the removal of sols can be facilitated by the addition of a suitable hydrolyzable metal salt. The resultant process, microflotation, has the same advantages as precipitate flotation. The particles are removed more rapidly and less selectively than would be possible without the addition of the hydrolyzable metal.

Studies with Titanium Dioxide

Titanium dioxide (TiO_2) is used as a filler and brightner in high quality paper and as a white pigment for paints. As a consequence of the manufacturing process it is commonly present in the waste effluents of these and related industries. Crystalline TiO_2 has an extremely small particle size of 0.1 to 0.4 microns and forms a negatively charged sol in aqueous media. Because of its colloidal properties and high refractive index, about 2.55, titanium dioxide forms very stable suspensions in dilute concentrations having an intense white to blue color. This study was undertaken first because of its practical implications and second because TiO_2 represents a completely different colloidal system than has been studied previously. Suspensions of the sol were prepared as described elsewhere (Rubin and Kovac, unpublished; Rubin and Haberkost, in preparation).

Several studies with TiO_2 were run in which the effects of pH, frother, coagulant and collector were observed. As expected, it was found that pH is very important and that removals are greatly affected by the aluminum sulfate (alum) concentration. The results indicated that collector concentration is a more important variable with TiO_2 than has been observed in other sol flotation studies. It was also found that the ethanol frother must be maintained at relatively high concentrations and that below some limiting dose flotation is significantly depressed. The role of frother is producing small bubbles of large specific surface area has been discussed (Rubin, et al., 1966; Rubin and Lackey, 1968). For the studies described here the ethanol dose was kept constant at 1.25 ml/l and the effects of aluminum sulfate and collector concentrations were examined in detail as a function of solution pH. The collectors chosen for the study were sodium lauryl sulfate (NaLS) and hexadecyltrimethylammonium bromide

(CTAB).

The effect of pH on 20 minute removals without alum or other aggregating agents (i.e., colloid flotation) using 20 mg/l sodium lauryl sulfate is summarized in Figure 19. Removals at this particular collector concentration were excellent in the pH range 2 to 3.3; above pH 4 the anionic collector was incapable of floating TiO_2 . Similar experiments were run at several NaLS concentrations to define its interrelationship with pH. The upper and lower pH limits, as estimated by 90% removals from data shown in Figure 19 and similar results, are plotted in Figure 20. This figure not only describes the shift of the removal zone toward lower pH as the collector concentration is increased, but also indicates that further increases above 60 mg/l would result in a stably dispersed, presumably hydrophilic sol resistant to removal by colloid flotation. It is interesting that the pH range of removal is increased as the collector dose is decreased so that the center of the removal zone is just above pH 3 at the lower limiting concentration of CTAB. This value agrees very well with the isoelectric point for TiO_2 as determined by streaming current measurements (Waters Streaming Current Detector) in the absence of surfactant or other chemicals.

Microflotation studies using the same collector were performed at a single alum dose of 50 mg/l as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The results of this series of experiments are summarized in Figure 21 which indicates the effect of the coagulant on the extent and rate of removal throughout the pH range of observation. The removals are in general agreement with observations on other sol systems that have been studied. At pH 2, where aluminum is completely soluble, and thus has little effect on the system, the rate and extent of removal are very similar to those found in the colloid flotation studies. Increasing the pH beyond pH 4.7 resulted in aluminum hydroxide precipitation, as

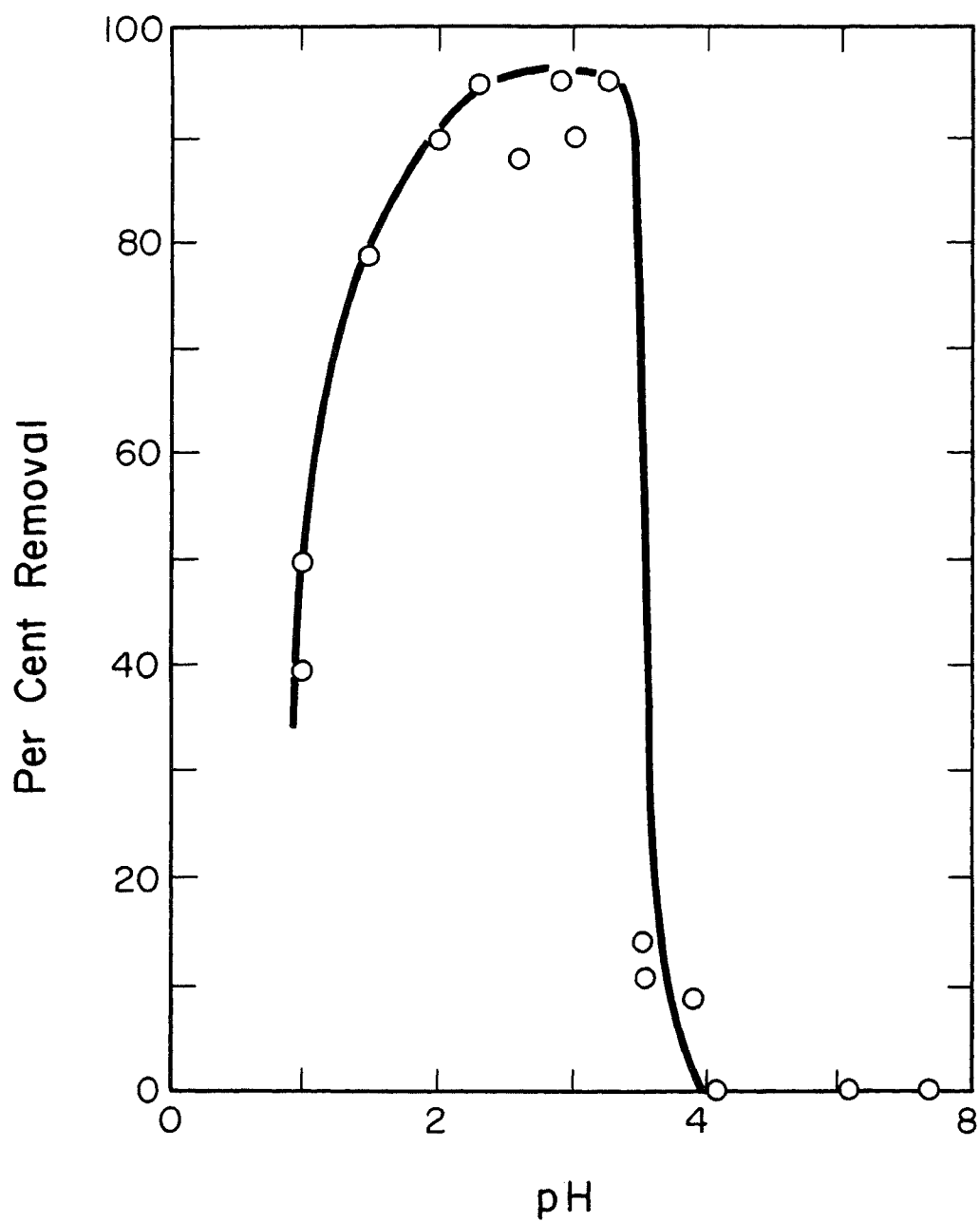


Figure 19 Effect of pH on the colloid flotation of TiO_2 with 30 mg/l NaLS. 20 minute removals at a gas flow rate of 19 ml/min. 1.25 ml/l Ethanol.

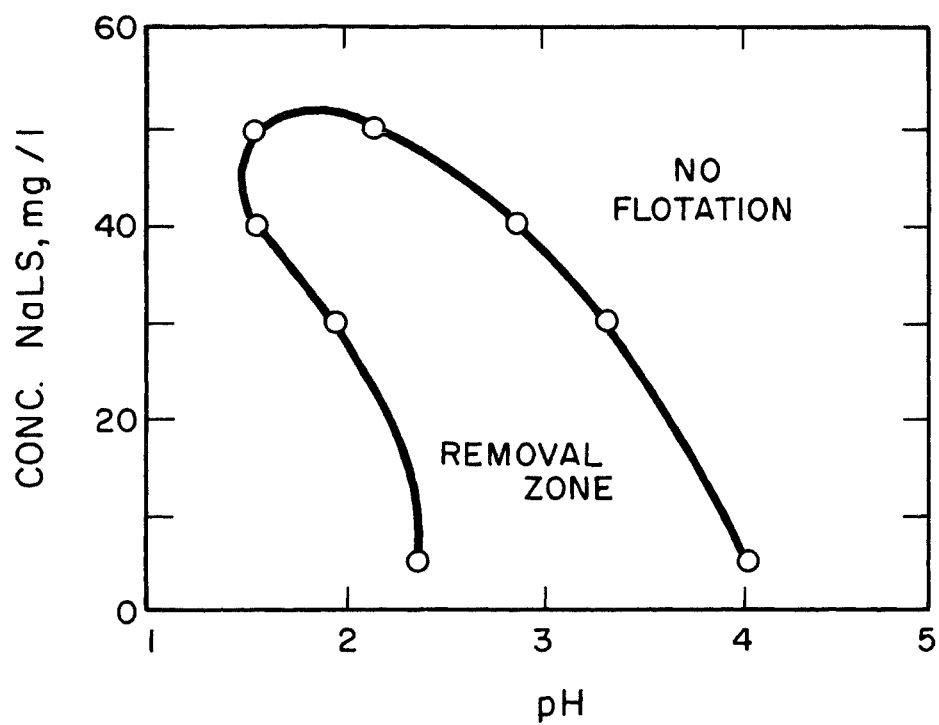


Figure 20 Effect of NaLS concentration on the pH range of 90% removal of TiO_2 by colloid flotation.

indicated by the dashed vertical lines in Figure 21, and removals were significantly enhanced. Both the rate of removal and its magnitude were greatest between pH 7 and 8 which corresponds to the range of maximum precipitation of freshly prepared aluminum hydroxide. As expected, removals were sharply decreased at the upper pH limit of precipitation; that is, upon dissolution of aluminum hydroxide to form the soluble aluminate ion.

Results of studies on the colloid flotation of TiO_2 using the cationic collector CTAB are summarized in the next two figures. The effects of several concentrations of this surfactant on 20-minute removals are shown as a function of pH in Figure 22. As with NaLS there are discrete pH ranges of removal depending on collector dose. At 5 and 10 mg/l flotation efficiency was sharply reduced above pH 9. In alkaline solutions with these low collector concentrations the foam was very unstable enabling any floated sol to be redispersed into the bulk liquid. In general, the zone of efficient removal by colloid flotation shifted toward higher pH as the CTAB dose was increased. This is in direct contrast to the results just described for the anionic collector which had the opposite effect (Figure 20). Linear extrapolation of the steep portions of the curves to 100% removal provides a consistent means of determining the limiting pH values needed to define the zone of efficient colloid with CTAB. This data, represented by open circles, is given in Figure 23. Thus, for example, at pH 10 colloid flotation occurs at any CTAB dose between about 10 and 50 mg/l. Higher doses are incapable of effectively floating the sol unless the pH is also increased.

It was observed that CTAB had the effect of coagulating or restabilizing ("peptizing") the TiO_2 sol. Consequently, several coagulation - settling experiments were run at several CTAB concentrations to differentiate between the surfactant as

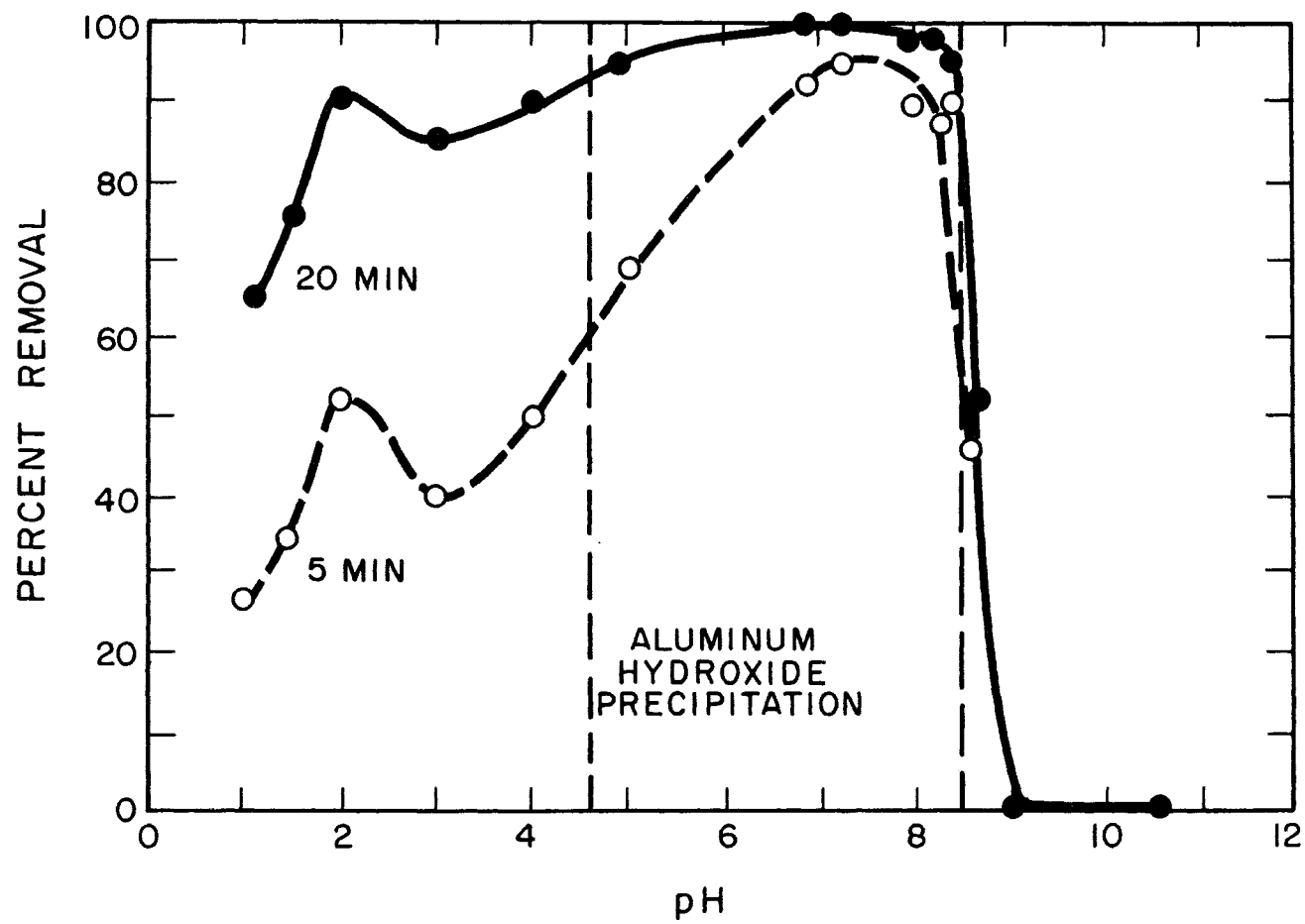


Figure 21 Effect of pH on microflotation of TiO_2 with 30 mg/l NaLS and 50 mg/l ALUM.

a coagulant or as a collector. The results of this study are also summarized in Figure 23. The open squares form the boundaries of the pH--CTAB concentration zone of destabilization. As indicated by the data the limiting pH of coagulation increased with increasing concentration of the cationic surfactant. CTAB concentrations greater than those along the line resulted in sol restabilization apparently through charge reversal. This phenomenon is well documented in the literature. At pH 6, for example, 10 mg/l of the collector just coagulates the sol while at 20 mg/l TiO_2 is still coagulated but no longer floatable. Upon dosing to 40 mg/l the sol, through adsorption of surfactant cations, becomes positively charged and colloiddally dispersed once again. In the absence of surfactant the sol is also coagulated, presumably by hydrogen ions, at pH just below pH 5. This is indicated in the figure by the point at zero CTAB to the left of the zone labeled "stable negative sol." From these results it is obvious that surfactant concentration is a significant parameter when attempting to float titanium dioxide.

The microflotation of TiO_2 using CTAB at several coagulant doses was also investigated. As shown in Figure 24 the addition of 50 mg/l alum did not have a significant effect on the pH range of removal at a collector concentration of 36.9 mg/l (compare with Figure 22). However, the rate of removal at pH 8 was increased. This pH corresponds to the isoelectric point of freshly prepared aluminum hydroxide as determined by streaming current measurements; at lower pH the insoluble hydroxide is colloiddally dispersed having a positive charge (Hayden, 1971). This effect, the non-floatability of positively charged sol when using a cationic collector was observed in similar studies with illite (Rubin and Erickson, 1970).

In general, it can be concluded that strongly ionized anionic surfactants such

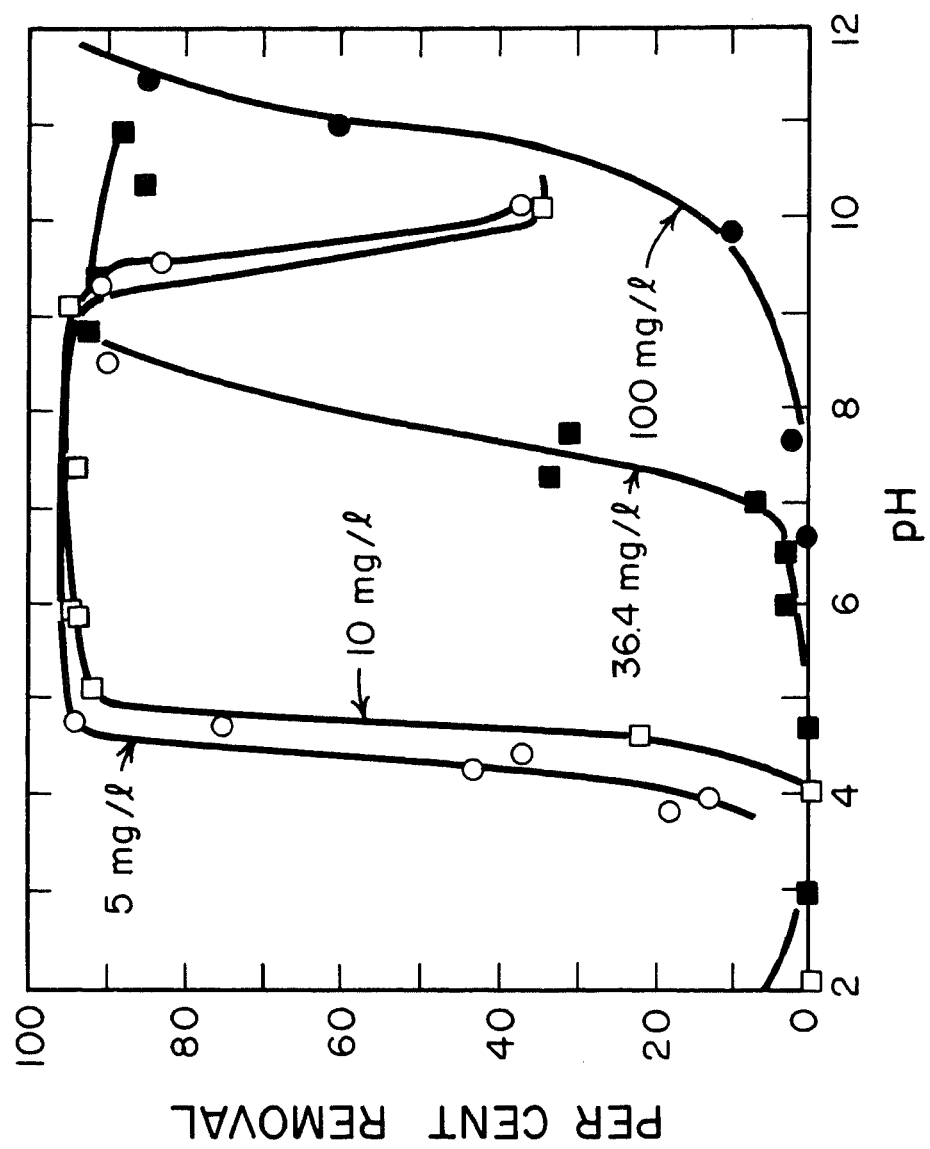


Figure 22 Effect of pH on colloid flotation of TiO_2 with CTAB.

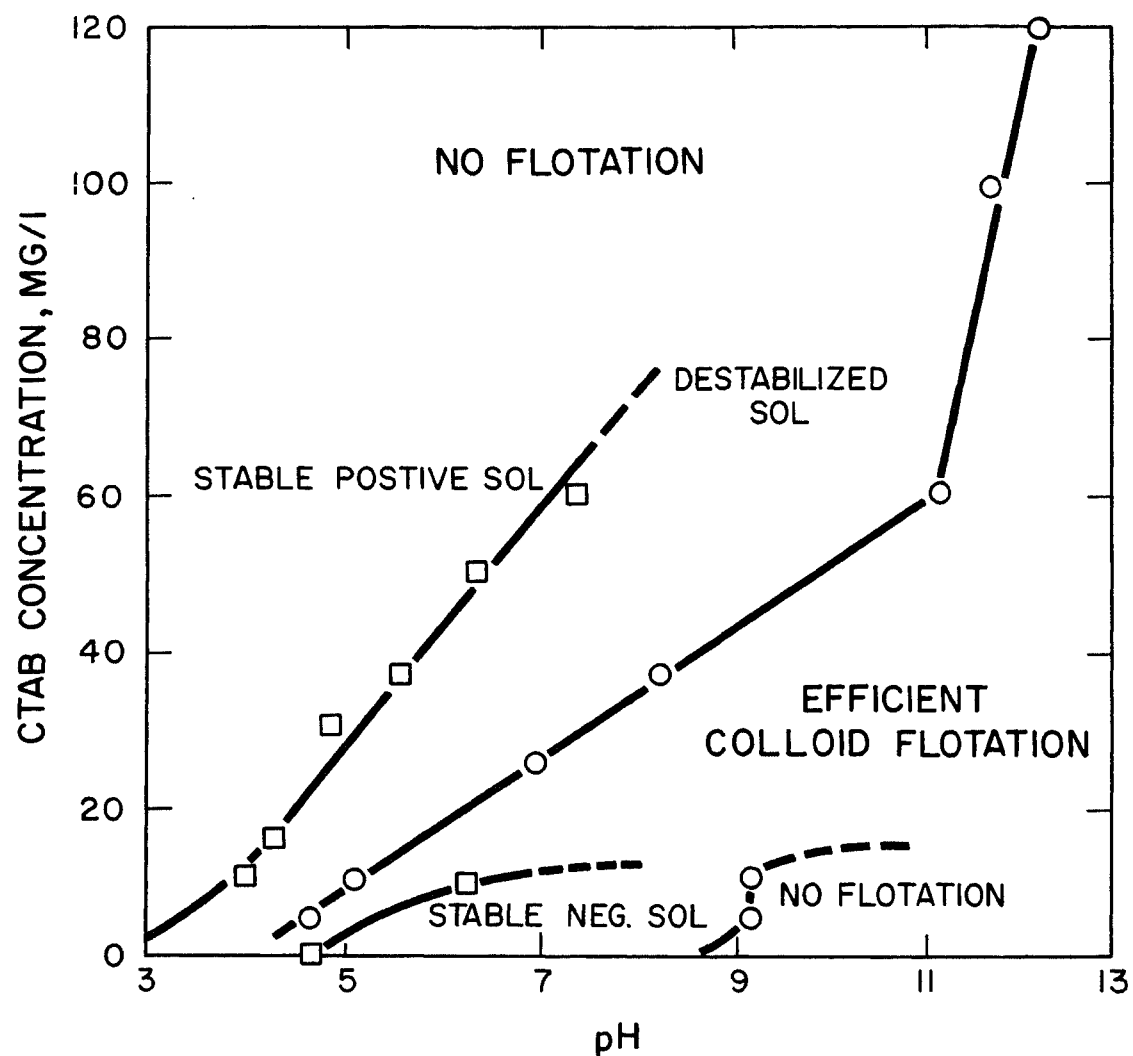


Figure 23 Effect of CTAB Concentration on Settleability and Colloid Flotation of Titanium Dioxide

as sodium lauryl sulfate are more effective collectors with microflotation. On the other hand, since most natural sols are negatively charged, it could be concluded that strongly ionized cationics such as CTAB are better suited for use with colloid flotation. With the proper conditions and in the pH range of aluminum hydroxide precipitation microflotation results in a more rapid and generally more efficient removal process that is less sensitive to surfactant concentration. When attempting colloid flotation it is very important that the effect of collector concentration be taken into account.

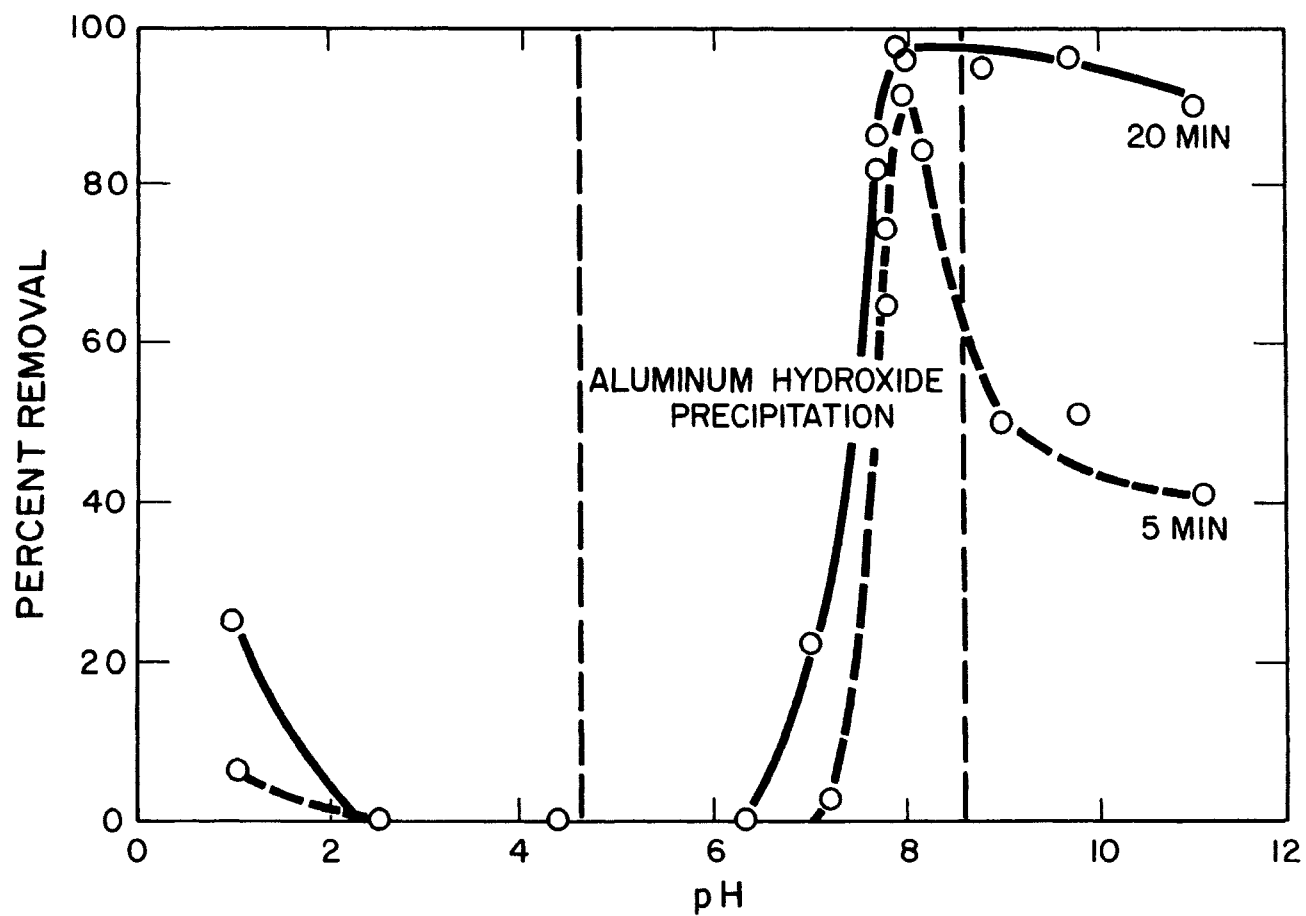


Figure 24 Effect of pH on the Microflotation of TiO_2 with 36.4 mg/l CTAB and 50 mg/l Alum. Shown also is the pH range of aluminum hydroxide precipitation.

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